

N Identical Particles Under Quantum Confinement: A Many-Body Dimensional Perturbation Theory Approach II, The Lowest-Order Wave Function II

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Abstract

In this paper, the second in a series of two, we complete the derivation of the lowest-order wave function of a dimensional perturbation theory (DPT) treatment for the N -body quantum-confined system. Taking advantage of the symmetry of the zeroth-order configuration, we use group theoretic techniques and the FG matrix method from quantum chemistry to obtain analytic results for frequencies and normal modes. This method directly accounts for each two-body interaction, rather than an average interaction so that even lowest-order results include beyond-mean-field effects. It is thus appropriate for the study of both weakly and strongly interacting systems and the transition between them. While previous work has focused on energies, lowest-order wave functions yield important information such as the nature of excitations and expectation values of physical observables at low orders including density profiles. Higher orders in DPT also require as input the zeroth-order wave functions. In the earlier paper we presented a program for calculating the analytic normal-mode coordinates of the large- D system and illustrated the procedure by deriving the two simplest normal modes. In this paper we complete this analysis by deriving the remaining, and more complex, normal coordinates of the system.

1 Introduction

Quantum confined systems involving N identical particles are common in many areas of physics, including chemical, condensed matter and atomic physics. In earlier papers[1, 2, 3] we have developed the method of dimensional perturbation theory[4] at low orders to examine the energies of quantum-confined systems such as atoms, quantum dots and Bose-Einstein condensates, both the ground and excited states. Dimensional perturbation theory (DPT) has many advantages. These include the fact that the number of particles,

N , enters into the theory as a parameter, and so it is easy to calculate results for an arbitrary number of particles. Also the theory is a beyond-mean-field method, directly accounting for each interaction, rather than some average representation of the interactions. It is therefore appropriate for confined systems of both weakly interacting and strongly interacting particles. In the case of a trapped gaseous atomic Bose-Einstein condensate (BEC) the system is typically a weakly interacting system for which a mean-field approximation is valid. However, if N is increased, or Feshbach resonances are exploited to increase the effective scattering length, or the system is squeezed in one or more directions, it will transition into a strongly-interacting regime where the mean-field approach breaks down. Such systems have been created in the laboratory.[5] Dimensional perturbation theory is equally applicable to both regimes and may be used to study the transition from weak to strongly interacting regimes. Even at lowest order DPT includes beyond-mean-field effects.

In an earlier paper[2] we presented a detailed discussion of the dimensional continuation of the N -particle Schrödinger equation, the $D \rightarrow \infty$ equilibrium (D^0) structure, and the energy through order D^{-1} . We used the FG matrix method to derive general, analytical expressions for the many-body normal-mode vibrational frequencies, and we gave specific analytical results for three confined N -body quantum systems: the N -electron atom, N -electron quantum dot, and N -atom inhomogeneous Bose-Einstein condensate with a repulsive hardcore potential.

In a subsequent paper[3] we studied the N -atom inhomogeneous Bose-Einstein condensate (BEC) with a repulsive hardcore potential, optimizing our low-order DPT energy by fitting to low- N diffusion Monte Carlo data[6] and then calculated results out to large N . Results were obtained for weak, intermediate and strong interatomic interactions.

Low-order many-body dimensional perturbation methods have been applied to the N -electron atom in Ref. [1] where analytical expressions are obtained for the ground-state energy of neutral atoms. For $Z = 1$ to 127, the energies compare well to Hartree-Fock energies with a correlation correction.

In a subsequent paper[7] (Paper I) we have begun a detailed derivation of the zeroth-order DPT wave function for quantum-confined systems

With the wave function many more properties of the system become accessible. The normal-mode coordinates of the zeroth-order wave function reveal the nature of the excitations of the system, and the lowest-order wave function provides expectation values and transition matrix elements to zeroth order in DPT. For macroscopic quantum-confined systems, such as the BEC, the wave function is manifested in an explicit way as the density profile may be viewed directly in the laboratory. This is readily calculable at zeroth order in DPT from the zeroth-order wave function.

Calculating energies and wave functions to higher orders in $1/D$ also requires as input the lowest-order wave function. Indeed, as we have discussed in an earlier paper[3] which considers energies and excitation frequencies of the BEC, low-order DPT calculations of confined interacting particles, including strongly interacting systems, are accurate out to N equals a few thousand particles. To obtain yet more accurate

energies, and to extend the calculation beyond a few thousand particles we need to go beyond these low-order calculations of the energies and excitation frequencies. These calculations are facilitated by Paper I and the present paper since, as we have already noted above, it requires the zeroth-order DPT wave function. This will be pursued in later papers.

In Paper I we set up the general theory for determining the zeroth-order DPT wave function of a quantum confined system. For quantum-confined systems in large dimensions, the Jacobian-weighted[8] wave function is harmonic, the system oscillating about a configuration termed the Lewis structure with every particle equidistant and equiangular from every other particle. Notwithstanding its relatively simple form, the large-dimension, zeroth-order wave function includes beyond-mean-field effects. The Lewis structure is a completely symmetric configuration invariant under a point group which is isomorphic to the symmetric group S_N . Using group theory associated with this S_N symmetry[9] and the FG matrix method familiar from quantum chemistry[10], there is a remarkable reduction from $N(N+1)/2$ possible distinct frequencies to only five distinct frequencies. The S_N symmetry also greatly simplifies the determination of the normal coordinates. There are five sets of normal coordinates, where the normal modes of a set have the same frequency and transform under the same irreducible representation of S_N . Two sets of normal coordinates transform under the $[N]$ irreducible representation, two sets of normal coordinates transform under the $[N-1, 1]$ irreducible representation, and one set of normal coordinates transforms under the $[N-2, 2]$ irreducible representation.

In Paper I we illustrated this general theory, for the zeroth-order DPT wave function of a quantum confined system, by determining the breathing and center-of-mass modes of the $[N]$ species (coordinates transforming under the same irreducible representation are said to belong to the same species). In this paper, we complete this analysis by determining the modes of the more complex $[N-1, 1]$ and $[N-2, 2]$ species. The zeroth-order density profile of the ground-state condensate is relatively simple to calculate once the zeroth-order wave function is known.

Paper I and this paper are restricted to consideration of quantum confined systems with a confining potential of spherical symmetry. The extension of this method to systems with cylindrical symmetry is relatively straightforward and will be discussed in subsequent papers. This is particularly important for the BEC as few current laboratory traps have spherical symmetry.

In Sections 2 through 7 we briefly review the general theory of the zeroth-order DPT wave function for a quantum confined system from Paper I. In contrast to Paper I where we first discussed the symmetry coordinates which motivated the introduction of the primitive irreducible coordinates, in this paper we lay out the steps involved sequentially in the order in which they are applied to a particular problem. In Section 8 we begin the extension to the $[N-1, 1]$ and $[N-2, 2]$ species by discussing the primitive irreducible coordinates for both the angular and radial sectors of these species. Angular and radial symmetry coordinates for the $[N-1, 1]$ and $[N-2, 2]$ species are then derived by forming appropriate linear combinations of the primitive irreducible coordinates. In Section 9 the frequencies and normal-mode coordinates of the system are derived

by transforming the \mathbf{G} and \mathbf{FG} matrices in the internal displacement coordinate basis to the symmetry coordinate basis. The problem is simplified by an extraordinary degree to two 2×2 and one 1×1 matrix eigenvalue equations. This reduction for $[N]$ species has already been discussed in Paper I. Here we focus on the remaining, more complicated $[N - 1, 1]$ and $[N - 2, 2]$ species. From the solution of these reduced eigenvalue equations, the $[N - 1, 1]$ and $[N - 2, 2]$ species normal coordinates are derived in Section 9.2. In Section 9.3 the normal mode motions of the particles in the original internal coordinates are derived. Section 10 and Section 11 summarize and conclude this paper.

2 The D -dimensional N -body Schrödinger Equation

In Paper I we considered an N -body system of particles confined by a spherically symmetric potential and interacting via a common two-body potential g_{ij} . The Schrödinger equation for this system in D -dimensional Cartesian coordinates is

$$H\Psi = \left[\sum_{i=1}^N h_i + \sum_{i=1}^{N-1} \sum_{j=i+1}^N g_{ij} \right] \Psi = E\Psi, \quad (1)$$

where

$$h_i = -\frac{\hbar^2}{2m_i} \sum_{\nu=1}^D \frac{\partial^2}{\partial x_{i\nu}^2} + V_{\text{conf}} \left(\sqrt{\sum_{\nu=1}^D x_{i\nu}^2} \right), \quad (2)$$

$$\text{and } g_{ij} = V_{\text{int}} \left(\sqrt{\sum_{\nu=1}^D (x_{i\nu} - x_{j\nu})^2} \right) \quad (3)$$

are the single-particle Hamiltonian and the two-body interaction potential, respectively. The operator H is the D -dimensional Hamiltonian, and $x_{i\nu}$ is the ν^{th} Cartesian component of the i^{th} particle. V_{conf} is the confining potential.

2.1 The Effective S -Wave Schrödinger Equation.

Restricting our attention to spherically symmetric ($L = 0$) states of the many-body system, we transform from Cartesian to internal coordinates. A convenient internal coordinate system for confined systems is

$$r_i = \sqrt{\sum_{\nu=1}^D x_{i\nu}^2} \quad (1 \leq i \leq N) \quad \text{and} \quad \gamma_{ij} = \cos(\theta_{ij}) = \left(\sum_{\nu=1}^D x_{i\nu} x_{j\nu} \right) / r_i r_j \quad (1 \leq i < j \leq N), \quad (4)$$

which are the D -dimensional scalar radii r_i of the N particles from the center of the confining potential and the cosines γ_{ij} of the $N(N-1)/2$ angles between the radial vectors. Under this coordinate change the effective S -wave Schrödinger equation in these internal coordinates becomes

$$\left[\sum_i \left\{ -\frac{\hbar^2}{2m_i} \left(\frac{\partial^2}{\partial r_i^2} + \frac{D-1}{r_i} \frac{\partial}{\partial r_i} + \sum_{j \neq i} \sum_{k \neq i} \frac{\gamma_{jk} - \gamma_{ij}\gamma_{ik}}{r_i^2} \frac{\partial^2}{\partial \gamma_{ij} \partial \gamma_{ik}} \right. \right. \right. \\ \left. \left. \left. - \frac{D-1}{r_i^2} \sum_{j \neq i} \gamma_{ij} \frac{\partial}{\partial \gamma_{ij}} \right) + V_{\text{conf}}(r_i) \right\} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N V_{\text{int}}(r_{ij}) \right] \Psi = E\Psi, \quad (5)$$

where $(r_{ij})^2 = (r_i)^2 + (r_j)^2 - 2r_i r_j \gamma_{ij}$.

2.2 The Jacobian-Weighted Schrödinger Equation

Dimensional perturbation theory utilizes a similarity transformation so that the kinetic energy operator is transformed into a sum of two types of terms, namely, derivative terms *and* a repulsive centrifugal-like term. The latter repulsive centrifugal-like term stabilizes the system against collapse in the large- D limit when attractive interparticle potentials are present. The zeroth and first orders of the dimensional ($1/D$) expansion of the similarity-transformed Schrödinger equation are then exactly soluble for any value of N . In the $D \rightarrow \infty$ limit, the derivative terms drop out, resulting in a static problem at zeroth order, while first order corrections correspond to simple-harmonic normal-mode oscillations about the infinite-dimensional structure.

In Paper I the weight function was chosen to be the square root of the inverse of the Jacobian, J , where[8]

$$J = (r_1 r_2 \dots r_N)^{D-1} \Gamma^{(D-N-1)/2} \quad (6)$$

and Γ is the Gramian determinant, the determinant of the matrix whose elements are γ_{ij} (see Appendix B of Paper I), so that the similarity-transformed wave function ${}_{(i)}\Phi$ and operators ${}_{(i)}\tilde{O}$ are

$${}_{(i)}\Phi = J^{\frac{1}{2}} \Psi, \text{ and } {}_{(i)}\tilde{O} = J^{\frac{1}{2}} \hat{O} J^{-\frac{1}{2}}. \quad (7)$$

Under this Jacobian transformation, a first derivative of an internal coordinate is the conjugate momentum to that coordinate. The matrix elements of coordinates and their derivatives between the zeroth-order normal-mode functions, which are involved in the development of higher-order DPT expansions, are much easier to calculate since the weight function in the integrals is now unity.

Carrying out the transformation of the Schrödinger equation of Eq. (1) via Eqs. (6) and (7), we obtain[8]:

$$({}_{(i)}T + V) {}_{(i)}\Phi = E {}_{(i)}\Phi, \quad (8)$$

where

$$\begin{aligned} {}_{(i)}T &= \hbar^2 \sum_{i=1}^N \left[-\frac{1}{2m_i} \frac{\partial^2}{\partial r_i^2} - \frac{1}{2m_i r_i^2} \left(\sum_{j \neq i} \sum_{k \neq i} (\gamma_{jk} - \gamma_{ij} \gamma_{ik}) \frac{\partial^2}{\partial \gamma_{ij} \partial \gamma_{ik}} - N \sum_{j \neq i} \gamma_{ij} \frac{\partial}{\partial \gamma_{ij}} \right) \right. \\ &\quad \left. + \frac{N(N-2) + (D-N-1)^2 \left(\frac{\Gamma^{(i)}}{\Gamma} \right)}{8m_i r_i^2} \right] \\ &= \hbar^2 \sum_{i=1}^N \left[-\frac{1}{2m_i} \frac{\partial^2}{\partial r_i^2} - \frac{1}{2m_i r_i^2} \sum_{j \neq i} \sum_{k \neq i} \frac{\partial}{\partial \gamma_{ij}} (\gamma_{jk} - \gamma_{ij} \gamma_{ik}) \frac{\partial}{\partial \gamma_{ik}} \right. \\ &\quad \left. + \frac{N(N-2) + (D-N-1)^2 \left(\frac{\Gamma^{(i)}}{\Gamma} \right)}{8m_i r_i^2} \right], \end{aligned} \quad (9)$$

and

$$V = \sum_{i=1}^N V_{\text{conf}}(r_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N V_{\text{int}}(r_{ij}). \quad (10)$$

The latter expression for ${}_{(i)}T$ is explicitly self-adjoint since the weight function, W , for the matrix elements is equal to unity. The similarity-transformed Hamiltonian for the energy eigenstate ${}_{(i)}\Phi$ is ${}_{(i)}H = ({}_{(i)}T + V)$.

3 Infinite- D analysis: Leading order energy

As in Paper I, we begin the perturbation analysis by regularizing the large-dimension limit of the Schrödinger equation by defining dimensionally-scaled variables:

$$\bar{r}_i = r_i/\kappa(D) \quad , \quad \bar{E} = \kappa(D)E \quad \text{and} \quad \bar{H} = \kappa(D) \quad {}_{(i)}H \quad (11)$$

where $\kappa(D)$ is a dimension-dependent scale factor. From Eq. (9) the kinetic energy T scales in the same way as $1/r^2$, so the scaled version of Eq. (8) becomes

$$\bar{H}\Phi = \left(\frac{1}{\kappa(D)}\bar{T} + \bar{V}_{\text{eff}} \right) \Phi = \bar{E}\Phi, \quad (12)$$

where barred quantities indicate that the variables are now in scaled units. The centrifugal-like term in T of Eq. (9) has quadratic D dependence so the scale factor $\kappa(D)$ must also be quadratic in D , otherwise the $D \rightarrow \infty$ limit of the Hamiltonian would not be finite. The precise form of $\kappa(D)$ depends on the particular system and is chosen so that the result of the scaling is as simple as possible. In previous work[2] we have chosen $\kappa(D) = (D-1)(D-2N-1)/(4Z)$ for the S -wave, N -electron atom; Ωl_{ho} for the N -electron quantum dot where $\Omega = (D-1)(D-2N-1)/4$ and the dimensionally-scaled harmonic oscillator length and trap frequency respectively are $l_{\text{ho}} = \sqrt{\frac{\hbar}{m^* \bar{\omega}_{\text{ho}}}}$ and $\bar{\omega}_{\text{ho}}^2 = \Omega^3 \omega_{\text{ho}}^2$; and $D^2 \bar{a}_{\text{ho}}$ for the BEC where $\bar{a}_{\text{ho}} = \sqrt{\frac{\hbar}{m \bar{\omega}_{\text{ho}}}}$ and $\bar{\omega}_{\text{ho}} = D^3 \omega_{\text{ho}}$. The factor of $\kappa(D)$ in the denominator of Eq. (12) suppresses the derivative terms as D increases leaving behind a centrifugal-like term in an effective potential,

$$\bar{V}_{\text{eff}}(\bar{r}, \gamma; \delta = 0) = \sum_{i=1}^N \left(\frac{\hbar^2}{8m_i \bar{r}_i^2} \frac{\Gamma^{(i)}}{\Gamma} + \bar{V}_{\text{conf}}(\bar{r}, \gamma; \delta = 0) \right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \bar{V}_{\text{int}}(\bar{r}, \gamma; \delta = 0), \quad (13)$$

with $\delta = 1/D$, in which the particles become frozen at large D . In the $D \rightarrow \infty$ ($\delta \rightarrow 0$) limit, the excited states collapse onto the ground state at the minimum of V_{eff} .

We assume a totally symmetric minimum characterized by the equality of all radii and angle cosines of the particles when $D \rightarrow \infty$, i.e.

$$\bar{r}_i = \bar{r}_{\infty} \quad (1 \leq i \leq N), \quad \gamma_{ij} = \bar{\gamma}_{\infty} \quad (1 \leq i < j \leq N). \quad (14)$$

In scaled units the zeroth-order ($D \rightarrow \infty$) approximation for the energy becomes

$$\bar{E}_{\infty} = \bar{V}_{\text{eff}}(\bar{r}_{\infty}, \bar{\gamma}_{\infty}; \delta = 0). \quad (15)$$

In this leading order approximation, the centrifugal-like term that appears in \bar{V}_{eff} , even for the ground state, is a zero-point energy contribution satisfying the minimum uncertainty principle[11].

4 Normal-mode analysis and the $1/D$ first-order quantum energy correction

At zeroth-order, the particles are frozen in a completely symmetric, high- D configuration which is somewhat analogous to the Lewis structure in atomic physics terminology. Similarly, the first-order $1/D$ correction can be viewed as small oscillations of this structure, analogous to Langmuir oscillations. To obtain the $1/D$ quantum correction to the energy for large but finite values of D , we expand about the minimum of the $D \rightarrow \infty$ effective potential. We first define a position vector, consisting of all $N(N+1)/2$ internal coordinates:

$$\bar{\mathbf{y}} = \begin{pmatrix} \bar{\mathbf{r}} \\ \boldsymbol{\gamma} \end{pmatrix}, \quad (16)$$

where

$$\bar{\mathbf{r}} = \begin{pmatrix} \bar{r}_1 \\ \bar{r}_2 \\ \vdots \\ \bar{r}_N \end{pmatrix} \quad (17)$$

and

$$\boldsymbol{\gamma} = \begin{pmatrix} \gamma_{12} \\ \gamma_{13} \\ \gamma_{23} \\ \gamma_{14} \\ \gamma_{24} \\ \gamma_{34} \\ \gamma_{15} \\ \gamma_{25} \\ \vdots \\ \gamma_{N-2,N} \\ \gamma_{N-1,N} \end{pmatrix}. \quad (18)$$

Making the following substitutions for all radii and angle cosines:

$$\bar{r}_i = \bar{r}_\infty + \delta^{1/2} \bar{r}'_i \quad (19)$$

$$\gamma_{ij} = \bar{\gamma}_\infty + \delta^{1/2} \bar{\gamma}'_{ij}, \quad (20)$$

where $\delta = 1/D$ is the expansion parameter, we define a displacement vector consisting of the internal displacement coordinates [primed in Eqs. (19) and (20)]

$$\bar{\mathbf{y}}' = \begin{pmatrix} \bar{\mathbf{r}}' \\ \bar{\boldsymbol{\gamma}}' \end{pmatrix}, \quad (21)$$

where

$$\bar{\mathbf{r}}' = \begin{pmatrix} \bar{r}'_1 \\ \bar{r}'_2 \\ \vdots \\ \bar{r}'_N \end{pmatrix}, \quad (22)$$

and

$$\bar{\boldsymbol{\gamma}}' = \begin{pmatrix} \bar{\gamma}'_{12} \\ \bar{\gamma}'_{13} \\ \bar{\gamma}'_{23} \\ \bar{\gamma}'_{14} \\ \bar{\gamma}'_{24} \\ \bar{\gamma}'_{34} \\ \bar{\gamma}'_{15} \\ \bar{\gamma}'_{25} \\ \vdots \\ \bar{\gamma}'_{N-2,N} \\ \bar{\gamma}'_{N-1,N} \end{pmatrix}. \quad (23)$$

We find

$$\bar{V}_{\text{eff}}(\bar{\mathbf{y}}'; \delta) = [\bar{V}_{\text{eff}}]_{\delta^{1/2}=0} + \frac{1}{2}\delta \left\{ \sum_{\mu=1}^P \sum_{\nu=1}^P \bar{y}'_{\mu} \left[\frac{\partial^2 \bar{V}_{\text{eff}}}{\partial \bar{y}_{\mu} \partial \bar{y}_{\nu}} \right]_{\delta^{1/2}=0} \bar{y}'_{\nu} + v_o \right\} + O(\delta^{3/2}), \quad (24)$$

where

$$P \equiv N(N+1)/2 \quad (25)$$

is the number of internal coordinates and v_o is a constant which comes from the explicit δ dependence in the centrifugal term. The first term of the $O((\delta^{1/2})^2)$ term defines the elements of the Hessian matrix[12] \mathbf{F} of Eq. (27) below. The derivative terms in the kinetic energy are taken into account by a similar series expansion, beginning with a first-order term that is bilinear in $\partial/\partial \bar{\mathbf{y}}'$, i.e.

$$\mathcal{T} = -\frac{1}{2}\delta \sum_{\mu=1}^P \sum_{\nu=1}^P G_{\mu\nu} \partial_{\bar{y}'_{\mu}} \partial_{\bar{y}'_{\nu}} + O(\delta^{3/2}), \quad (26)$$

where \mathcal{T} is the derivative portion of the kinetic energy T [see Eq. (9)]. It follows from Eqs. (24) and (26) that \mathbf{G} and \mathbf{F} , both constant matrices, are defined in the first-order $\delta = 1/D$ Hamiltonian as follows:

$$\hat{H}_1 = -\frac{1}{2}\partial_{\bar{\mathbf{y}}'}^T \mathbf{G} \partial_{\bar{\mathbf{y}}'} + \frac{1}{2}\bar{\mathbf{y}}'^T \mathbf{F} \bar{\mathbf{y}}' + v_o. \quad (27)$$

Thus, obtaining the first-order energy correction is reduced to a harmonic problem, which is solved by obtaining the normal modes of the system.

We use the FG matrix method[13] to obtain the normal-mode vibrations and, thereby, the first-order energy correction. A derivation of the FG matrix method may be found in Appendix A of Paper I, but the

main results may be stated as follows. The b^{th} normal mode coordinate may be written as:

$$[\mathbf{q}']_b = \mathbf{b}^T \bar{\mathbf{y}}', \quad (28)$$

where the coefficient vector \mathbf{b} satisfies the eigenvalue equation,

$$\mathbf{F} \mathbf{G} \mathbf{b} = \lambda_b \mathbf{b}, \quad (29)$$

with the resultant secular equation

$$\det(\mathbf{F} \mathbf{G} - \lambda \mathbf{I}) = 0. \quad (30)$$

The coefficient vector also satisfies the normalization condition

$$\mathbf{b}^T \mathbf{G} \mathbf{b} = 1. \quad (31)$$

The frequencies $\bar{\omega}_b^2$ are related to λ by:

$$\lambda_b = \bar{\omega}_b^2, \quad (32)$$

while the wave function is a product of $P = N(N+1)/2$ harmonic oscillator wave functions

$$\Phi_0(\bar{\mathbf{y}}') = \prod_{b=1}^P h_{n_b} \left(\bar{\omega}_b^{1/2} [\mathbf{q}']_b \right), \quad (33)$$

where $h_{n_b} \left(\bar{\omega}_b^{1/2} [\mathbf{q}']_b \right)$ is a one-dimensional harmonic-oscillator wave function of frequency $\bar{\omega}_b$, and n_b is the oscillator quantum number, $0 \leq n_b < \infty$, which counts the number of quanta in each normal mode.

In an earlier paper[2] we solve Eqs. (30) and (32) for the frequencies. The number of roots λ of Eq. (30) – there are $P \equiv N(N+1)/2$ roots – is potentially huge. However, due to the S_N symmetry of the problem discussed in Sect. 5 of Paper I, there is a stunning simplification. Equation (30) has only five distinct roots, λ_μ , where μ runs over $\mathbf{0}^-$, $\mathbf{0}^+$, $\mathbf{1}^-$, $\mathbf{1}^+$, and $\mathbf{2}$, regardless of the number of particles in the system (see Refs. [2] and Sect. 7.5). Thus the energy through first-order (see Eq. (35)) can be written in terms of the five distinct normal-mode vibrational frequencies which are related to the roots λ_μ of FG by

$$\lambda_\mu = \bar{\omega}_\mu^2. \quad (34)$$

The energy through first-order in $\delta = 1/D$ is then[2]

$$\bar{E} = \bar{E}_\infty + \delta \left[\sum_{\mu=\{\mathbf{0}^\pm, \mathbf{1}^\pm, \mathbf{2}\}} \sum_{n_\mu=0}^{\infty} (n_\mu + \frac{1}{2}) d_{\mu, n_\mu} \bar{\omega}_\mu + v_o \right], \quad (35)$$

where the n_μ are the vibrational quantum numbers of the normal modes with the same frequency $\bar{\omega}_\mu$. The quantity d_{μ, n_μ} is the occupancy of the manifold of normal modes with vibrational quantum number n_μ and normal mode frequency $\bar{\omega}_\mu$. The total occupancy of the normal modes with frequency $\bar{\omega}_\mu$ is equal to the multiplicity of the root λ_μ , i.e.

$$d_\mu = \sum_{n_\mu=0}^{\infty} d_{\mu, n_\mu}, \quad (36)$$

where d_μ is the multiplicity of the μ^{th} root. The multiplicities of the five roots are [2]

$$\begin{aligned}
d_{\mathbf{0}+} &= 1, \\
d_{\mathbf{0}-} &= 1, \\
d_{\mathbf{1}+} &= N-1, \\
d_{\mathbf{1}-} &= N-1, \\
d_{\mathbf{2}} &= N(N-3)/2.
\end{aligned} \tag{37}$$

Note that although the equation in Ref. [1] for the energy through Langmuir order is the same as Eq. (35), it is expressed a little differently (See Ref. [14]).

5 The Symmetry of the Large- D , N -body Quantum Confinement Problem

5.1 Q matrices in terms of simple invariant submatrices

Such a high degree of degeneracy of the frequencies in large- D , N -body quantum confinement problem indicates a high degree of symmetry. The \mathbf{F} , \mathbf{G} , and \mathbf{FG} matrices, which we generically denote by \mathbf{Q} , are $P \times P$ matrices. The S_N symmetry of the \mathbf{Q} matrices (\mathbf{F} , \mathbf{G} , and \mathbf{FG}) allows us to write these matrices in terms of six simple submatrices which are invariant under S_N . We first define the number of γ_{ij} coordinates to be

$$M \equiv N(N-1)/2, \tag{38}$$

and let \mathbf{I}_N be an $N \times N$ identity matrix, \mathbf{I}_M an $M \times M$ identity matrix, \mathbf{J}_N an $N \times N$ matrix of ones and \mathbf{J}_M an $M \times M$ matrix of ones. Further, we let \mathbf{R} be an $N \times M$ matrix such that $R_{i,jk} = \delta_{ij} + \delta_{ik}$, \mathbf{J}_{NM} be an $N \times M$ matrix of ones, and $\mathbf{J}_{NM}^T = \mathbf{J}_{MN}$. These matrices are invariant under interchange of the particles, the S_N symmetry, and form a closed algebra (see Appendix B of Ref. [2]).

We can then write the \mathbf{Q} matrices as

$$\mathbf{Q} = \begin{pmatrix} \mathbf{Q}_{\bar{\mathbf{r}}'\bar{\mathbf{r}}'} & \mathbf{Q}_{\bar{\mathbf{r}}'\bar{\boldsymbol{\gamma}}'} \\ \mathbf{Q}_{\bar{\boldsymbol{\gamma}}'\bar{\mathbf{r}}'} & \mathbf{Q}_{\bar{\boldsymbol{\gamma}}'\bar{\boldsymbol{\gamma}}'} \end{pmatrix}, \tag{39}$$

where the block $\mathbf{Q}_{\bar{\mathbf{r}}'\bar{\mathbf{r}}'}$ has dimension $(N \times N)$, block $\mathbf{Q}_{\bar{\mathbf{r}}'\bar{\boldsymbol{\gamma}}'}$ has dimension $(N \times M)$, block $\mathbf{Q}_{\bar{\boldsymbol{\gamma}}'\bar{\mathbf{r}}'}$ has dimension $(M \times N)$, and block $\mathbf{Q}_{\bar{\boldsymbol{\gamma}}'\bar{\boldsymbol{\gamma}}'}$ has dimension $(M \times M)$. Now, as we show in Appendix B of Ref. [2], we can write the \mathbf{Q} matrices as follows:

$$\mathbf{Q}_{\bar{\mathbf{r}}'\bar{\mathbf{r}}'} = (Q_a - Q_b)\mathbf{I}_N + Q_b\mathbf{J}_N \tag{40}$$

$$\mathbf{Q}_{\bar{\mathbf{r}}'\bar{\boldsymbol{\gamma}}'} = (Q_e - Q_f)\mathbf{R} + Q_f\mathbf{J}_{NM} \tag{41}$$

$$\mathbf{Q}_{\bar{\boldsymbol{\gamma}}'\bar{\mathbf{r}}'} = (Q_c - Q_d)\mathbf{R}^T + Q_d\mathbf{J}_{NM}^T \tag{42}$$

$$\mathbf{Q}_{\bar{\boldsymbol{\gamma}}'\bar{\boldsymbol{\gamma}}'} = (Q_g - 2Q_h + Q_i)\mathbf{I}_M + (Q_h - Q_i)\mathbf{R}^T\mathbf{R} + Q_i\mathbf{J}_M. \tag{43}$$

It is this structure that results in the remarkable reduction from a possible $P = N(N + 1)/2$ distinct frequencies to just five distinct frequencies.

For $\mathbf{Q} = \mathbf{F}\mathbf{G}$, the matrix that must be diagonalized in Eq. (29), Eq. (39) becomes

$$\mathbf{F}\mathbf{G} = \begin{pmatrix} \tilde{a}\mathbf{I}_N + \tilde{b}\mathbf{J}_N & \tilde{e}\mathbf{R} + \tilde{f}\mathbf{J}_{NM} \\ \tilde{c}\mathbf{R}^T + \tilde{d}\mathbf{J}_{MN} & \tilde{g}\mathbf{I}_M + \tilde{h}\mathbf{R}^T\mathbf{R} + \tilde{i}\mathbf{J}_M \end{pmatrix}, \quad (44)$$

where we have used the following abbreviations:

$$\begin{aligned} \tilde{a} &\equiv (FG)_a - (FG)_b = (F_a - F_b)G_a \\ \tilde{b} &\equiv (FG)_b = F_b G_a \\ \tilde{c} &\equiv (FG)_c - (FG)_d = (F_e - F_f)G_a \\ \tilde{d} &\equiv (FG)_d = F_f G_a \\ \tilde{e} &\equiv (FG)_e - (FG)_f = (F_e - F_f)(G_g + (N - 4)G_h) \\ \tilde{f} &\equiv (FG)_f = 2F_e G_h + F_f(G_g + 2(N - 3)G_h) \\ \tilde{g} &\equiv (FG)_g - 2(FG)_h + (FG)_\iota = (F_g - 2F_h + F_\iota)(G_g - 2G_h) \\ \tilde{h} &\equiv (FG)_h - (FG)_\iota = F_g G_h + F_h(G_g + (N - 6)G_h) - F_\iota(G_g + (N - 5)G_h) \\ \tilde{i} &\equiv (FG)_\iota = 4F_h G_h + F_\iota(G_g + 2(N - 4)G_h). \end{aligned} \quad (45)$$

The \mathbf{F} and \mathbf{G} matrix elements on the right-hand sides of Eq. (45) may be derived using the graph-theoretic techniques discussed in Appendix B of Ref. [2].

We also require the \mathbf{G} matrix for the normalization condition (Eq. (31)). It has a simpler structure than the $\mathbf{F}\mathbf{G}$ matrix,

$$\mathbf{G} = \begin{pmatrix} \tilde{a}'\mathbf{I}_N & \mathbf{0} \\ \mathbf{0} & \tilde{g}'\mathbf{I}_M + \tilde{h}'\mathbf{R}^T\mathbf{R} \end{pmatrix}, \quad (46)$$

where

$$\begin{aligned} \tilde{a}' &\equiv (G)_a \\ \tilde{g}' &\equiv (G)_g - 2(G)_h \\ \tilde{h}' &\equiv (G)_h \end{aligned} \quad (47)$$

and

$$\begin{aligned} (G)_b &= 0 \\ (G)_c &= 0 \\ (G)_d &= 0 \\ (G)_e &= 0 \\ (G)_f &= 0 \\ (G)_\iota &= 0. \end{aligned} \quad (48)$$

The quantities $(G)_a$, $(G)_g$ and $(G)_h$ depend on the choice of $\kappa(D)$ (See Ref. [2]).

6 Symmetry and Normal Coordinates

As discussed in Paper I the \mathbf{FG} matrix is a $N(N+1)/2 \times N(N+1)/2$ dimensional matrix (there being $N(N+1)/2$ internal coordinates), and so Eqs. (29) and (30) could have up to $N(N+1)/2$ distinct frequencies. However, as noted above, there are only five distinct frequencies. The S_N symmetry is responsible for the remarkable reduction from $N(N+1)/2$ possible distinct frequencies to five actual distinct frequencies. As we shall also see, the S_N symmetry greatly simplifies the determination of the normal coordinates and hence the solution of the large- D problem.

6.1 Symmetrized coordinates

The \mathbf{Q} matrices, and in particular the \mathbf{FG} matrix, are invariants under S_N , so they do not connect subspaces belonging to different irreducible representations of S_N [10]. Thus from Eqs. (28) and (29) the normal coordinates must transform under irreducible representations of S_N . Since the normal coordinates will be linear combinations of the elements of the internal coordinate displacement vectors $\bar{\mathbf{r}}'$ and $\bar{\boldsymbol{\gamma}}'$, we first look at the S_N transformation properties of the internal coordinates.

The internal coordinate displacement vectors $\bar{\mathbf{r}}'$ and $\bar{\boldsymbol{\gamma}}'$ of Eqs. (22) and (23) are basis functions which transform under matrix representations of S_N , and each span the corresponding carrier spaces, however these representations of S_N are not irreducible representations of S_N .

In Sec. 6.1 of Paper I we have shown that the reducible representation under which $\bar{\mathbf{r}}'$ transforms is reducible to one 1-dimensional irreducible representation labelled by the partition $[N]$ (the partition denotes a corresponding Young diagram (= Young pattern = Young shape) of an irreducible representation (see Appendix C of Paper I) and one $(N-1)$ -dimensional irreducible representation labelled by the partition $[N-1, 1]$. We also showed in Sec 6.1 of Paper I that the reducible representation under which $\bar{\boldsymbol{\gamma}}'$ transforms is reducible to one 1-dimensional irreducible representation labelled by the partition $[N]$, one $(N-1)$ -dimensional irreducible representation labelled by the partition $[N-1, 1]$ and one $N(N-3)/2$ -dimensional irreducible representation labelled by the partition $[N-2, 2]$. Thus if d_α is the dimensionality of the irreducible representation of S_N denoted by the partition α then

$$\begin{aligned} d_{[N]} &= 1 \\ d_{[N-1, 1]} &= N-1 \\ d_{[N-2, 2]} &= \frac{N(N-3)}{2} \end{aligned} \tag{49}$$

and so

$$d_{[N]} + d_{[N-1, 1]} = N, \tag{50}$$

giving correctly the dimension of the $\bar{\mathbf{r}}'$ vector and that

$$d_{[N]} + d_{[N-1, 1]} + d_{[N-2, 2]} = \frac{N(N-1)}{2}, \quad (51)$$

giving correctly the dimension of the $\bar{\boldsymbol{\gamma}}'$ vector.

Since the normal modes transform under irreducible representations of S_N and are composed of linear combinations of the elements of the internal coordinate displacement vectors $\bar{\mathbf{r}}'$ and $\bar{\boldsymbol{\gamma}}'$, there will be two 1-dimensional irreducible representations labelled by the partition $[N]$, two $(N-1)$ -dimensional irreducible representations labelled by the partition $[N-1, 1]$ and one entirely angular $N(N-3)/2$ -dimensional irreducible representation labelled by the partition $[N-2, 2]$. Thus if we look at Eq. (37) we see that the $\mathbf{0}^\pm$ normal modes transform under two $[N]$ irreducible representations, the $\mathbf{1}^\pm$ normal modes transform under two $[N-1, 1]$ irreducible representations, while the $\mathbf{2}$ normal modes transform under the $[N-2, 2]$ irreducible representation.

7 Calculating the Normal Modes.

7.1 An Outline of the Program to Calculate the Normal Modes of the System.

Summarizing the procedure in Paper I, we determine the normal coordinates in a three-step process:

- a). We determine the primitive irreducible coordinates by the following procedure. First, we determine two sets of linear combinations of the elements of coordinate vector $\bar{\mathbf{r}}'$ which transform under particular non-orthogonal $[N]$ and $[N-1, 1]$ irreducible representations of S_N . Using these two sets of coordinates we then determine two sets of linear combinations of the elements of coordinate vector $\bar{\boldsymbol{\gamma}}'$ which transform under exactly the same non-orthogonal $[N]$ and $[N-1, 1]$ irreducible representations of S_N as the coordinate sets in the $\bar{\mathbf{r}}'$ sector. Finally, another set of linear combinations of the elements of coordinate vector $\bar{\boldsymbol{\gamma}}'$ which transforms under a particular non-orthogonal $[N-2, 2]$ irreducible representation of S_N is determined. In particular we set out to find sets of coordinates transforming irreducibly under S_N which have the simplest functional form possible subject to the requirement that they transform irreducibly under S_N . We call these coordinates primitive irreducible coordinates.
- b). Appropriate linear combinations within each coordinate set from item a). above are taken so that the results transform under orthogonal irreducible representations of S_N . These are then the symmetry coordinates of the problem[13]. Care is taken to ensure that the transformation from the coordinates which transform under the non-orthogonal irreducible representations of S_N of item a). above, to the symmetry coordinates which transform under orthogonal irreducible representations of S_N preserve the identity of equivalent representations in the $\bar{\mathbf{r}}'$ and $\bar{\boldsymbol{\gamma}}'$ sectors. Furthermore, we choose one of the symmetry coordinates to be just a single primitive irreducible

coordinate so that it has the simplest functional form possible under the requirement that it transforms irreducibly under S_N . The succeeding symmetry coordinate is then chosen to be composed of two primitive irreducible coordinates and so on. In this way the complexity of the functional form of the symmetry coordinates is kept to a minimum and only builds up slowly as more symmetry coordinates of a given species are considered.

- c). The \mathbf{FG} matrix is expressed in the $\bar{\mathbf{r}}'$, $\bar{\boldsymbol{\gamma}}'$ basis. However, if we change the basis in which the \mathbf{FG} matrix is expressed to the symmetry coordinates an enormous simplification occurs. The $N(N+1)/2 \times N(N+1)/2$ eigenvalue equation of Eq. (29) is reduced to one 2×2 eigenvalue equation for the $[N]$ sector, $N-1$ identical 2×2 eigenvalue equations for the $[N-1, 1]$ sector and $N(N-3)/2$ identical 1×1 eigenvalue equations for the $[N-2, 2]$ sector. In the case of the 2×2 eigenvalue equations for the $[N]$ and $[N-1, 1]$ sectors, the 2×2 structure allows for the mixing in the normal coordinates of the symmetry coordinates in the $\bar{\mathbf{r}}'$ and $\bar{\boldsymbol{\gamma}}'$ sectors. The 1×1 structure of the eigenvalue equations in the $[N-2, 2]$ sector reflects the fact that there are no $[N-2, 2]$ symmetry coordinates in the $\bar{\mathbf{r}}'$ sector for the $[N-2, 2]$ symmetry coordinates in the $\bar{\boldsymbol{\gamma}}'$ sector to couple with. The $[N-2, 2]$ normal modes are entirely angular.

7.2 The Primitive Irreducible Coordinate Vectors $\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}$ and $\bar{\mathbf{S}}_{\bar{\boldsymbol{\gamma}}'}$.

The primitive irreducible coordinates, $\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}$, of the $\bar{\mathbf{r}}'$ sector which transform under irreducible, though non-orthogonal, representations of the group S_N are given by

$$\bar{\mathbf{S}}_{\bar{\mathbf{r}}'} = \bar{\mathbf{W}}_{\bar{\mathbf{r}}'} \bar{\mathbf{r}}', \quad (52)$$

where

$$\bar{\mathbf{W}}_{\bar{\mathbf{r}}'} = \begin{pmatrix} \bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N]} \\ \bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]} \end{pmatrix}, \quad (53)$$

$\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N]}$ is a $1 \times N$ dimensional matrix and $\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}$ is an $(N-1) \times N$ dimensional matrix. Hence we can write

$$\bar{\mathbf{S}}_{\bar{\mathbf{r}}'} = \begin{pmatrix} \bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N]} \\ \bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]} \end{pmatrix} = \begin{pmatrix} \bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N]} \bar{\mathbf{r}}' \\ \bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]} \bar{\mathbf{r}}' \end{pmatrix}. \quad (54)$$

Likewise the primitive irreducible coordinates, $\bar{\mathbf{S}}_{\bar{\boldsymbol{\gamma}}'}$, of the $\bar{\boldsymbol{\gamma}}'$ sector which transform under irreducible, though non-orthogonal, representations of the group S_N are given by

$$\bar{\mathbf{S}}_{\bar{\boldsymbol{\gamma}}'} = \bar{\mathbf{W}}_{\bar{\boldsymbol{\gamma}}'} \bar{\boldsymbol{\gamma}}' \quad (55)$$

and so writing

$$\bar{\mathbf{W}}_{\bar{\boldsymbol{\gamma}}'} = \begin{pmatrix} \bar{\mathbf{W}}_{\bar{\boldsymbol{\gamma}}'}^{[N]} \\ \bar{\mathbf{W}}_{\bar{\boldsymbol{\gamma}}'}^{[N-1, 1]} \\ \bar{\mathbf{W}}_{\bar{\boldsymbol{\gamma}}'}^{[N-2, 2]} \end{pmatrix}, \quad (56)$$

where $\overline{W}_{\overline{\gamma}'}^{[N]}$ is a $1 \times N(N-1)/2$ dimensional matrix, $\overline{W}_{\overline{\gamma}'}^{[N-1, 1]}$ is an $(N-1) \times N(N-1)/2$ dimensional matrix and $\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}$ is an $N(N-3)/2 \times N(N-1)/2$ dimensional matrix, then

$$\overline{S}_{\overline{\gamma}'} = \begin{pmatrix} \overline{S}_{\overline{\gamma}'}^{[N]} \\ \overline{S}_{\overline{\gamma}'}^{[N-1, 1]} \\ \overline{S}_{\overline{\gamma}'}^{[N-2, 2]} \end{pmatrix} = \begin{pmatrix} \overline{W}_{\overline{\gamma}'}^{[N]} \overline{\gamma}' \\ \overline{W}_{\overline{\gamma}'}^{[N-1, 1]} \overline{\gamma}' \\ \overline{W}_{\overline{\gamma}'}^{[N-2, 2]} \overline{\gamma}' \end{pmatrix}, \quad (57)$$

where

$$\overline{W}_{\overline{\gamma}'}^{\alpha} \overline{\gamma}' = \sum_{j=1}^N \sum_{i < j} [\overline{W}_{\overline{\gamma}'}^{\alpha}]_{ij} \overline{\gamma}'_{ij}. \quad (58)$$

7.3 The Full Primitive Irreducible Coordinate Vector, \overline{S} .

It is useful to form a full primitive irreducible coordinate vector that groups primitive irreducible coordinates of the same species together as follows:

$$\overline{S} = P \begin{pmatrix} \overline{S}_{\overline{r}'} \\ \overline{S}_{\overline{\gamma}'} \end{pmatrix} = \begin{pmatrix} \overline{S}_{\overline{r}'}^{[N]} \\ \overline{S}_{\overline{\gamma}'}^{[N]} \\ \overline{S}_{\overline{r}'}^{[N-1, 1]} \\ \overline{S}_{\overline{\gamma}'}^{[N-1, 1]} \\ \overline{S}_{\overline{r}'}^{[N-2, 2]} \\ \overline{S}_{\overline{\gamma}'}^{[N-2, 2]} \end{pmatrix} = \begin{pmatrix} \overline{S}^{[N]} \\ \overline{S}^{[N-1, 1]} \\ \overline{S}^{[N-2, 2]} \end{pmatrix}, \quad (59)$$

where the orthogonal matrix P is given by

$$P = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad (60)$$

and

$$\overline{S}^{[N]} = \begin{pmatrix} \overline{S}_{\overline{r}'}^{[N]} \\ \overline{S}_{\overline{\gamma}'}^{[N]} \end{pmatrix}, \quad \overline{S}^{[N-1, 1]} = \begin{pmatrix} \overline{S}_{\overline{r}'}^{[N-1, 1]} \\ \overline{S}_{\overline{\gamma}'}^{[N-1, 1]} \end{pmatrix} \quad \text{and} \quad \overline{S}^{[N-2, 2]} = \overline{S}_{\overline{\gamma}'}^{[N-2, 2]}. \quad (61)$$

Now consider applying a transformation \overline{W} to Eqs. (28), (29), (30) and (31), where

$$\overline{W} = P \left(\overline{W}_{\overline{r}'} \left| \begin{array}{c} \mathbf{0} \\ \overline{W}_{\overline{\gamma}'} \end{array} \right. \right) = \begin{pmatrix} \overline{W}_{\overline{r}'}^{[N]} & \mathbf{0} \\ \mathbf{0} & \overline{W}_{\overline{\gamma}'}^{[N]} \\ \overline{W}_{\overline{r}'}^{[N-1, 1]} & \mathbf{0} \\ \mathbf{0} & \overline{W}_{\overline{\gamma}'}^{[N-1, 1]} \\ \mathbf{0} & \overline{W}_{\overline{\gamma}'}^{[N-2, 2]} \end{pmatrix}, \quad (62)$$

where

$$\overline{S} = \overline{W} \overline{y}'. \quad (63)$$

We can now relate the primitive irreducible coordinate vector $\overline{\mathbf{S}}$ of Eq. (59) and item a). above, to the symmetry coordinate vector \mathbf{S} of item b). above.

7.4 The Transformation, U , from Primitive Irreducible Coordinates to Symmetry Coordinates.

The symmetry coordinate vector \mathbf{S} will be related to the primitive irreducible coordinate vector $\overline{\mathbf{S}}$ by a non-orthogonal linear transformation U , i.e.

$$\mathbf{S} = U \overline{\mathbf{S}}, \quad (64)$$

where

$$\mathbf{S} = \begin{pmatrix} \mathbf{S}_{\overline{\mathbf{r}}'}^{[N]} \\ \mathbf{S}_{\overline{\mathbf{r}}'}^{[N]} \\ \hline \mathbf{S}_{\overline{\mathbf{r}}'}^{[N-1, 1]} \\ \mathbf{S}_{\overline{\mathbf{r}}'}^{[N-1, 1]} \\ \hline \mathbf{S}_{\overline{\mathbf{r}}'}^{[N-2, 2]} \end{pmatrix} = \begin{pmatrix} \mathbf{S}^{[N]} \\ \mathbf{S}^{[N-1, 1]} \\ \mathbf{S}^{[N-2, 2]} \end{pmatrix} \quad (65)$$

and

$$\mathbf{S}^{[N]} = \begin{pmatrix} \mathbf{S}_{\overline{\mathbf{r}}'}^{[N]} \\ \mathbf{S}_{\overline{\mathbf{r}}'}^{[N]} \end{pmatrix}, \quad \mathbf{S}^{[N-1, 1]} = \begin{pmatrix} \mathbf{S}_{\overline{\mathbf{r}}'}^{[N-1, 1]} \\ \mathbf{S}_{\overline{\mathbf{r}}'}^{[N-1, 1]} \end{pmatrix} \quad \text{and} \quad \mathbf{S}^{[N-2, 2]} = \mathbf{S}_{\overline{\mathbf{r}}'}^{[N-2, 2]}. \quad (66)$$

In \mathbf{S} , symmetry coordinates of the same species are grouped together.

Defining W through the equation

$$\mathbf{S} = W \overline{\mathbf{y}}', \quad (67)$$

then Eqs. (59), (61), (62), (63), (65), (66) and (67) imply that W will be related to \overline{W} by the same transformation, i.e.

$$W = U \overline{W}, \quad (68)$$

where

$$U = \left(\begin{array}{cc|cc|c} U_{\overline{\mathbf{r}}'}^{[N]} & 0 & 0 & 0 & 0 \\ 0 & U_{\overline{\mathbf{r}}'}^{[N]} & 0 & 0 & 0 \\ \hline 0 & 0 & U_{\overline{\mathbf{r}}'}^{[N-1, 1]} & 0 & 0 \\ 0 & 0 & 0 & U_{\overline{\mathbf{r}}'}^{[N-1, 1]} & 0 \\ \hline 0 & 0 & 0 & 0 & U_{\overline{\mathbf{r}}'}^{[N-2, 2]} \end{array} \right), \quad (69)$$

so that

$$W = \left(\begin{array}{cc|c} W_{\overline{\mathbf{r}}'}^{[N]} & \mathbf{0} & \\ \mathbf{0} & W_{\overline{\mathbf{r}}'}^{[N]} & \\ \hline W_{\overline{\mathbf{r}}'}^{[N-1, 1]} & \mathbf{0} & \\ \mathbf{0} & W_{\overline{\mathbf{r}}'}^{[N-1, 1]} & \\ \hline \mathbf{0} & W_{\overline{\mathbf{r}}'}^{[N-2, 2]} & \end{array} \right) = \left(\begin{array}{cc|c} U_{\overline{\mathbf{r}}'}^{[N]} \overline{W}_{\overline{\mathbf{r}}'}^{[N]} & \mathbf{0} & \\ \mathbf{0} & U_{\overline{\mathbf{r}}'}^{[N]} \overline{W}_{\overline{\mathbf{r}}'}^{[N]} & \\ \hline U_{\overline{\mathbf{r}}'}^{[N-1, 1]} \overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]} & \mathbf{0} & \\ \mathbf{0} & U_{\overline{\mathbf{r}}'}^{[N-1, 1]} \overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]} & \\ \hline \mathbf{0} & U_{\overline{\mathbf{r}}'}^{[N-2, 2]} \overline{W}_{\overline{\mathbf{r}}'}^{[N-2, 2]} & \end{array} \right). \quad (70)$$

Thus we have

$$W_{\mathbf{X}'}^\alpha = U_{\mathbf{X}'}^\alpha \overline{W}_{\mathbf{X}'}^\alpha, \quad (71)$$

where \mathbf{X}' is $\bar{\mathbf{r}}'$ or $\bar{\boldsymbol{\gamma}}'$ (only $\bar{\boldsymbol{\gamma}}'$ for the $[N-2, 2]$ sector). According to item b). of Sec. 7.1 W is an orthogonal transformation, and so

$$W_{\mathbf{X}'}^\alpha [W_{\mathbf{X}'}^\alpha]^T = I_\alpha, \quad (72)$$

where I_α is the unit matrix.

Equation (72) is the *essential equation* for $W_{\mathbf{X}'}^\alpha$ to satisfy.

From Eqs. (21), (65), (67) and (70), one derives

$$\mathbf{S}_{\mathbf{X}'}^\alpha = W_{\mathbf{X}'}^\alpha \mathbf{X}', \quad (73)$$

where \mathbf{X}' is either of the $\bar{\mathbf{r}}'$ or $\bar{\boldsymbol{\gamma}}'$ internal displacement coordinate vectors and $\alpha \neq [N-2, 2]$ when $\mathbf{X}' = \bar{\mathbf{r}}'$.

According to Eqs. (71) and (72), $U_{\mathbf{X}'}^\alpha$ must satisfy

$$U_{\mathbf{X}'}^\alpha \left\{ \overline{W}_{\mathbf{X}'}^\alpha [\overline{W}_{\mathbf{X}'}^\alpha]^T \right\} [U_{\mathbf{X}'}^\alpha]^T = I_\alpha. \quad (74)$$

Thus to determine $U_{\mathbf{X}'}^\alpha$, we need to know $\overline{W}_{\mathbf{X}'}^\alpha [\overline{W}_{\mathbf{X}'}^\alpha]^T$ beforehand.

In accordance with item a). of Sec. 7.1, $\overline{\mathbf{S}}_{\bar{\boldsymbol{\gamma}}'}^\alpha$, where α is $[N]$ or $[N-1, 1]$, transforms under exactly the same representation of S_N as $\overline{\mathbf{S}}_{\bar{\mathbf{r}}'}^\alpha$. Likewise, according to item b). of Sec. 7.1, $\mathbf{S}_{\bar{\boldsymbol{\gamma}}'}^\alpha$ transforms under exactly the same representation of S_N as $\mathbf{S}_{\bar{\mathbf{r}}'}^\alpha$. Thus we must have

$$U_{\bar{\boldsymbol{\gamma}}'}^\alpha = A_U^\alpha U_{\bar{\mathbf{r}}'}^\alpha, \quad (75)$$

where α is $[N]$ or $[N-1, 1]$ and A_U^α is a number (see below). Note that Eq. (75) substituted in Eq. (74) yields:

$$\overline{W}_{\bar{\boldsymbol{\gamma}}'}^\alpha [\overline{W}_{\bar{\boldsymbol{\gamma}}'}^\alpha]^T = \frac{1}{(A_U^\alpha)^2} \overline{W}_{\bar{\mathbf{r}}'}^\alpha [\overline{W}_{\bar{\mathbf{r}}'}^\alpha]^T \quad (76)$$

when α is $[N]$ or $[N-1, 1]$.

7.4.1 The Motion Associated with the Symmetry Coordinates about the Lewis Structure Configuration.

Inverting Eq. (67) we get

$$\bar{\mathbf{y}}' = W^T \mathbf{S}, \quad (77)$$

where $\bar{\mathbf{y}}'$ is defined in Eqs. (21), (22) and (23), \mathbf{S} is given by Eqs. (65) and (66), and W is given by Eq. (70). Equation (77) may be directly derived from Eq. (67) using the orthogonality of the W matrix.

From Eq. (77) we can derive

$$\mathbf{y} = \begin{pmatrix} \mathbf{r} \\ \gamma \end{pmatrix} = \begin{pmatrix} D^2 \bar{a}_{ho} \left(\bar{\mathbf{r}}'_\infty \mathbf{1}_{\bar{\mathbf{r}}'} + \frac{1}{\sqrt{D}} \sum_{\alpha} \sum_{\xi} \bar{\mathbf{r}}'^{\alpha}_{\xi} \right) \\ \gamma_\infty \mathbf{1}_{\bar{\gamma}'} + \frac{1}{\sqrt{D}} \sum_{\alpha} \sum_{\xi} \bar{\gamma}'^{\alpha}_{\xi} \end{pmatrix} \quad (78)$$

where

$$\bar{\mathbf{r}}'^{\alpha}_{\xi} = [\mathbf{S}^{\alpha}_{\bar{\mathbf{r}}'}]_{\xi} [(W^{\alpha}_{\bar{\mathbf{r}}'})_{\xi}]^T, \quad (79)$$

$$\bar{\gamma}'^{\alpha}_{\xi} = [\mathbf{S}^{\alpha}_{\bar{\gamma}'}]_{\xi} [(W^{\alpha}_{\bar{\gamma}'})_{\xi}]^T, \quad (80)$$

while

$$[\mathbf{1}_{\bar{\mathbf{r}}'}]_i = 1 \quad \forall \quad 1 \leq i \leq N \quad (81)$$

and

$$[\mathbf{1}_{\bar{\gamma}'}]_{ij} = 1 \quad \forall \quad 1 \leq i, j \leq N. \quad (82)$$

Equations (78), (79), (80), (81) and (82) express the the motion associated with the symmetry coordinate about the Lewis structure configuration.

7.5 The Reduction of the Eigensystem Equations in the Symmetry Coordinate Basis .

7.5.1 The Central Theorem.

Defining \mathbf{Q}_W to be a \mathbf{Q} matrix in the symmetry coordinate basis, i.e.

$$\mathbf{Q}_W = W \mathbf{Q} W^T, \quad (83)$$

where \mathbf{Q} is \mathbf{F} , \mathbf{G} or \mathbf{FG} , and \mathbf{Q}_W is \mathbf{F}_W , \mathbf{G}_W or $(\mathbf{FG})_W$. Since \mathbf{F} , \mathbf{G} and \mathbf{FG} are invariant matrices (under S_N)[10], then

$$\mathbf{Q}_W = \begin{pmatrix} \sigma^Q_{[N]} \otimes \mathbf{I}_{[N]} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \sigma^Q_{[N-1, 1]} \otimes \mathbf{I}_{[N-1, 1]} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma^Q_{[N-2, 2]} \otimes \mathbf{I}_{[N-2, 2]} \end{pmatrix}, \quad (84)$$

where the symbol \otimes indicates the direct product, $\sigma^Q_{[N]}$ and $\sigma^Q_{[N-1, 1]}$ are 2×2 dimensional matrices and $\sigma^Q_{[N-2, 2]}$ is a single element (a number). The matrix $\mathbf{I}_{[N]}$ is the $[N]$ -sector identity matrix, simply the number 1, $\mathbf{I}_{[N-1, 1]}$ is the $[N-1, 1]$ -sector identity matrix, the $(N-1) \times (N-1)$ -dimensional unit matrix and $\mathbf{I}_{[N-2, 2]}$ is the $[N-2, 2]$ -sector identity matrix, the $N(N-3)/2 \times N(N-3)/2$ -dimensional unit matrix. The matrix elements

$$[\sigma^Q_{\alpha}]_{\mathbf{X}'_1, \mathbf{X}'_2} = (W^{\alpha}_{\mathbf{X}'_1})_{\xi} \mathbf{Q}_{\mathbf{X}'_1 \mathbf{X}'_2} [(W^{\alpha}_{\mathbf{X}'_2})_{\xi}]^T, \quad (85)$$

where \mathbf{X}'_1 and \mathbf{X}'_2 are $\bar{\mathbf{r}}'$ or $\bar{\mathbf{y}}'$ (only $\bar{\mathbf{y}}'$ for the $[N-2, 2]$ sector). The \mathbf{Q} -matrix quadrant, $\mathbf{Q}_{\mathbf{X}'_1 \mathbf{X}'_2}$, is given by Eqs. (39), (40), (41), (42) and (43). Although we are *not* summing over the repeated index ξ in Eq. (85), the $[\sigma_{\alpha}^{\mathbf{Q}}]_{\mathbf{X}'_1 \mathbf{X}'_2}$ are *independent* of the $W_{\mathbf{X}'}^{\alpha}$ row label, ξ . If, when we calculate $W_{\mathbf{X}'}^{\alpha}$, the matrix element $[\sigma_{\alpha}^{\mathbf{Q}}]_{\mathbf{X}'_1 \mathbf{X}'_2}$ turns out to depend on the $W_{\mathbf{X}'}^{\alpha}$ row label, ξ , then we know that we have made a mistake calculating $W_{\mathbf{X}'}^{\alpha}$. This is a strong check on the correctness of our calculations in Sect. 8.

7.5.2 The Reduction of the Eigenvalue Equation in the Symmetry Coordinate Basis.

As in Paper I, we transform the basic eigenvalue equation, Eq. (29), to the symmetry coordinate basis:

$$WFW^T WGW^T W\mathbf{b} = \mathbf{F}_W \mathbf{G}_W \mathbf{c}^{(b)} = \lambda_b \mathbf{c}^{(b)}, \quad (86)$$

where

$$\mathbf{F}_W = WFW^T, \quad \mathbf{G}_W = WGW^T \quad (87)$$

$$, \quad \mathbf{c}^{(b)} = W\mathbf{b}. \quad (88)$$

Using Eq. (28) the b^{th} normal-mode coordinate can be written under this transformation as:

$$[q']_b = \mathbf{b}^T W^T W \bar{\mathbf{y}}' = [\mathbf{c}^{(b)}]^T \cdot \mathbf{S}, \quad (89)$$

where $[q']_b$ is now directly expressed in terms of the symmetry coordinates.

The normal-coordinate coefficient vector, $\mathbf{c}^{(b)}$, has the form:

$$\mathbf{c}^{(b)} = \begin{pmatrix} \delta_{\alpha, [N]} \mathbf{c}^{[N]} \otimes \mathbf{1} \\ \delta_{\alpha, [N-1, 1]} \mathbf{c}^{[N-1, 1]} \otimes \mathbf{1}_{\xi}^{[N-1, 1]} \\ \delta_{\alpha, [N-2, 2]} \mathbf{c}^{[N-2, 2]} \otimes \mathbf{1}_{\xi}^{[N-2, 2]} \end{pmatrix}, \quad (90)$$

where we have used Eqs. (84) and (86), and the \mathbf{c}^{α} satisfy the eigenvalue equations

$$\sigma_{\alpha}^{FG} \mathbf{c}^{\alpha} = \lambda_{\alpha} \mathbf{c}^{\alpha}. \quad (91)$$

The $\sigma_{[N]}^{FG}$ and $\sigma_{[N-1, 1]}^{FG}$ are 2×2 -dimensional matrices, while $\sigma_{[N-2, 2]}^{FG}$ is a one-dimensional matrix. Thus there are five solutions to Eq. (91) denoted by $\{\lambda_{[N]}^{\pm}, \mathbf{c}_{\pm}^{[N]}\}$, $\{\lambda_{[N-1, 1]}^{\pm}, \mathbf{c}_{\pm}^{[N-1, 1]}\}$ and $\{\lambda_{[N-2, 2]}, \mathbf{c}^{[N-2, 2]}\}$, where \mathbf{X}' ($\bar{\mathbf{r}}'$ or $\bar{\mathbf{y}}'$, only $\bar{\mathbf{y}}'$ for the $[N-2, 2]$ sector) labels the rows of the elements of the column vector \mathbf{c}^{α} . The normal-coordinate label, b , has been replaced by the labels α , ξ and \pm on the right hand side of Eq. (90), while the elements of the column vectors $\mathbf{1}_{\xi}^{\alpha}$ are

$$[\mathbf{1}_{\xi}^{\alpha}]_{\eta} = \delta_{\xi\eta}, \quad (92)$$

with $1 \leq \xi, \eta \leq N-1$ when $\alpha = [N-1, 1]$, or $1 \leq \xi, \eta \leq N(N-3)/2$ when $\alpha = [N-2, 2]$. The $\mathbf{c}_{\pm}^{\alpha}$ vectors for the $[N]$ and $[N-1, 1]$ sectors determine the amount of angular-radial mixing between the symmetry coordinates in a normal coordinate of a particular α . For the $[N-2, 2]$ sector, the symmetry coordinates are the $[N-2, 2]$ sector normal coordinates up to a normalization constant, $[\mathbf{c}^{[N-2, 2]}]_{\bar{\mathbf{y}}'}$ (see Sec. 7.5.3).

Writing \mathbf{c}^α as

$$\mathbf{c}^\alpha = c^\alpha \times \widehat{\mathbf{c}}^\alpha, \quad (93)$$

where $\widehat{\mathbf{c}}^\alpha$ is a vector satisfying the normalization condition

$$[\widehat{\mathbf{c}}^\alpha]^T \widehat{\mathbf{c}}^\alpha = 1, \quad (94)$$

and c^α is a normalization factor ensuring that Eq. (31) is satisfied (see Sec. 7.5.3 below). Then the reduced eigenvalue equation, Eq. (91), determines $\widehat{\mathbf{c}}^\alpha$ alone.

With the $[N-2, 2]$ sector, Eq. (94) yields

$$\mathbf{c}^{[N-2, 2]} = 1, \quad (95)$$

and so Eq. (91) yields directly

$$\lambda_{[N-2, 2]} = \sigma_{[N-2, 2]}^{FG}. \quad (96)$$

For the $[N]$ and $[N-1, 1]$ sectors, if we write

$$\widehat{\mathbf{c}}_\pm^\alpha = \begin{pmatrix} \cos \theta_\pm^\alpha \\ \sin \theta_\pm^\alpha \end{pmatrix}, \quad (97)$$

then from Eqs. (89), (90), (93) and (97)

$$[q']_b = c_\pm^\alpha (\cos \theta_\pm^\alpha [\mathbf{S}_{\bar{r}'}^\alpha]_\xi + \sin \theta_\pm^\alpha [\mathbf{S}_{\bar{\gamma}'}^\alpha]_\xi). \quad (98)$$

Writing

$$\sigma_\alpha^{FG} = \begin{pmatrix} [\sigma_\alpha^{FG}]_{\bar{r}', \bar{r}'} & [\sigma_\alpha^{FG}]_{\bar{r}', \bar{\gamma}'} \\ [\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{r}'} & [\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{\gamma}'} \end{pmatrix}, \quad (99)$$

then Eq. (91) may be written as

$$\begin{pmatrix} ([\sigma_\alpha^{FG}]_{\bar{r}', \bar{r}'} - \lambda_\pm^\alpha) & [\sigma_\alpha^{FG}]_{\bar{r}', \bar{\gamma}'} \\ [\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{r}'} & ([\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{\gamma}'} - \lambda_\pm^\alpha) \end{pmatrix} \begin{pmatrix} \cos \theta_\pm^\alpha \\ \sin \theta_\pm^\alpha \end{pmatrix} = 0, \quad (100)$$

from which we derive the following analytic formula for the frequencies:

$$\lambda_\alpha^\pm = \frac{([\sigma_\alpha^{FG}]_{\bar{r}', \bar{r}'} + [\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{\gamma}'} \pm \sqrt{([\sigma_\alpha^{FG}]_{\bar{r}', \bar{r}'} - [\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{\gamma}'})^2 + 4[\sigma_\alpha^{FG}]_{\bar{r}', \bar{\gamma}'} [\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{r}'}}}{2} \quad (101)$$

Equations (100) and (101) then yield

$$\tan \theta_\pm^\alpha = \frac{(\lambda_\pm^\alpha - [\sigma_\alpha^{FG}]_{\bar{r}', \bar{r}'})}{[\sigma_\alpha^{FG}]_{\bar{r}', \bar{\gamma}'}} = \frac{[\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{r}'}}{(\lambda_\pm^\alpha - [\sigma_\alpha^{FG}]_{\bar{\gamma}', \bar{\gamma}'}), \quad (102)$$

7.5.3 The Normalization Condition.

Using Eqs. (31), (87), (84), (85) and (90), the \mathbf{c}^α also satisfy the normalization condition

$$[\mathbf{c}^\alpha]^T \sigma_\alpha^G \mathbf{c}^\alpha = 1. \quad (103)$$

From Eqs. (93) and (103):

$$c^\alpha = \frac{1}{\sqrt{[\widehat{\mathbf{c}}^\alpha]^T \boldsymbol{\sigma}_\alpha^G \widehat{\mathbf{c}}^\alpha}}. \quad (104)$$

For the $[N-2, 2]$ sector, Eqs. (95) and (104) yield

$$c^{[N-2, 2]} = \frac{1}{\sqrt{\boldsymbol{\sigma}_{[N-2, 2]}^G}}. \quad (105)$$

For the $[N]$ and $[N-1, 1]$ sectors, Eqs. (97) and (104) yield for the normalization constant, c_\pm^α

$$c_\pm^\alpha = \frac{1}{\sqrt{\begin{pmatrix} \cos \theta_\pm^\alpha \\ \sin \theta_\pm^\alpha \end{pmatrix}^T \boldsymbol{\sigma}_\alpha^G \begin{pmatrix} \cos \theta_\pm^\alpha \\ \sin \theta_\pm^\alpha \end{pmatrix}}}. \quad (106)$$

7.5.4 The Normal Coordinates.

The normal-coordinate vector, \mathbf{q}' , is given by

$$\begin{aligned} \mathbf{q}' &= \begin{pmatrix} \mathbf{q}'^{[N]} \\ \mathbf{q}'^{[N-1, 1]} \\ \mathbf{q}'^{[N-2, 2]} \end{pmatrix} = \begin{pmatrix} \frac{\mathbf{q}'_+^{[N]}}{\mathbf{q}'_-^{[N]}} \\ \frac{\mathbf{q}'_+^{[N-1, 1]}}{\mathbf{q}'_-^{[N-1, 1]}} \\ \frac{\mathbf{q}'_-^{[N-2, 2]}}{\mathbf{q}'_-^{[N-2, 2]}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{c_+^{[N]} \cos \theta_+^{[N]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N]} + c_+^{[N]} \sin \theta_+^{[N]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N]}}{c_+^{[N]} \cos \theta_-^{[N]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N]} + c_-^{[N]} \sin \theta_-^{[N]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N]}} \\ \frac{c_+^{[N-1, 1]} \cos \theta_+^{[N-1, 1]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]} + c_+^{[N-1, 1]} \sin \theta_+^{[N-1, 1]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]}}{c_-^{[N-1, 1]} \cos \theta_-^{[N-1, 1]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]} + c_-^{[N-1, 1]} \sin \theta_-^{[N-1, 1]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]}} \\ \frac{c_-^{[N-2, 2]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N-2, 2]}}{c_-^{[N-2, 2]} \mathbf{S}_{\bar{\mathbf{r}}'}^{[N-2, 2]}} \end{pmatrix}. \end{aligned} \quad (107)$$

7.5.5 The Motion Associated with the Normal Coordinates about the Lewis Structure Configuration.

In terms of the normal coordinates, the unscaled internal coordinate vector is

$$\mathbf{y} = \begin{pmatrix} \mathbf{r} \\ \gamma \end{pmatrix} = \mathbf{y}_\infty + \frac{1}{\sqrt{D}} \begin{pmatrix} \sum_{\alpha=\left\{\begin{smallmatrix} [N], \\ [N-1, 1] \end{smallmatrix}\right\}} \sum_{\xi} \sum_{\tau=\pm} \tau \mathbf{y}'_\xi{}^\alpha + \sum_{\xi} \mathbf{y}'_\xi{}^{[N-2, 2]} \end{pmatrix}, \quad (108)$$

where

$$\mathbf{y}_\infty = \begin{pmatrix} D^2 \bar{a}_{ho} \bar{\mathbf{r}}'_\infty \mathbf{1}_{\bar{\mathbf{r}}'} \\ \gamma_\infty \mathbf{1}_{\bar{\mathbf{r}}'} \end{pmatrix}, \quad (109)$$

with $\mathbf{1}_{\bar{\mathbf{r}}'}$ and $\mathbf{1}_{\bar{\boldsymbol{\gamma}}'}$ given by Eqs. (81) and (82) respectively. The vectors $+\mathbf{y}'_{\xi}{}^{\alpha}$, $-\mathbf{y}'_{\xi}{}^{\alpha}$ and $\mathbf{y}'_{\xi}{}^{[N-2, 2]}$ are

$$+\mathbf{y}'_{\xi}{}^{\alpha} = \frac{1}{s(\theta^{\alpha})} \begin{pmatrix} D^2 \bar{a}_{ho} \frac{-\sin \theta_{+}^{\alpha}}{c_{+}^{\alpha}} [\mathbf{q}'_{+}]_{\xi} [(W_{\bar{\mathbf{r}}'}^{\alpha})_{\xi}]^T \\ \frac{\cos \theta_{+}^{\alpha}}{c_{+}^{\alpha}} [\mathbf{q}'_{+}]_{\xi} [(W_{\bar{\boldsymbol{\gamma}}'}^{\alpha})_{\xi}]^T \end{pmatrix}, \quad (110)$$

$$-\mathbf{y}'_{\xi}{}^{\alpha} = \frac{1}{s(\theta^{\alpha})} \begin{pmatrix} D^2 \bar{a}_{ho} \frac{\sin \theta_{+}^{\alpha}}{c_{+}^{\alpha}} [\mathbf{q}'_{-}]_{\xi} [(W_{\bar{\mathbf{r}}'}^{\alpha})_{\xi}]^T \\ \frac{-\cos \theta_{+}^{\alpha}}{c_{+}^{\alpha}} [\mathbf{q}'_{-}]_{\xi} [(W_{\bar{\boldsymbol{\gamma}}'}^{\alpha})_{\xi}]^T \end{pmatrix} \quad (111)$$

for $\alpha = [N]$ or $[N-1, 1]$, and

$$\mathbf{y}'_{\xi}{}^{[N-2, 2]} = \begin{pmatrix} \mathbf{0} \\ \frac{1}{c^{[N-2, 2]}} [\mathbf{q}'^{[N-2, 2]}]_{\xi} [(W_{\bar{\boldsymbol{\gamma}}'}^{[N-2, 2]})_{\xi}]^T \end{pmatrix}. \quad (112)$$

Equations (108), (109), (110), (111) and (112) express, in terms of the internal coordinates \mathbf{r} and $\boldsymbol{\gamma}$, the motion associated with the normal coordinates, \mathbf{q}' , about the Lewis structure configuration \mathbf{y}_{∞} .

8 Symmetry Coordinates Belonging to the $[N-1, 1]$ and $[N-2, 2]$ Species.

The symmetry coordinates of $[N]$ species have been discussed in Sec. 7.6 of Paper I. Here we derive the symmetry coordinates of $[N-1, 1]$ and $[N-2, 2]$ species.

8.1 Symmetry Coordinates Belonging to the $[N-1, 1]$ Species.

8.1.1 The $\bar{\mathbf{r}}'$ Sector.

The Primitive Irreducible Coordinate. Consider the $N(N-1)$ quantities $\bar{r}'_i - \bar{r}'_j$ where $1 \leq i \neq j \leq N$. It's clear that under S_N they transform into themselves. However, they are not all linearly independent. As we shall justify below, we identify the $N-1$ linearly independent elements of $\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}$ as

$$[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i = \bar{r}'_i - \bar{r}'_{i+1} \quad \text{where} \quad 1 \leq i \leq N-1, \quad (113)$$

a subset of the $N(N-1)$ $\bar{r}'_i - \bar{r}'_j$. Obviously

$$\bar{r}'_j - \bar{r}'_i = -(\bar{r}'_i - \bar{r}'_j) \quad (114)$$

so we can restrict ourselves to the $\bar{r}'_i - \bar{r}'_j$ for which $i \leq j$. Furthermore we can write

$$\bar{r}'_i - \bar{r}'_{i+a} = \sum_{\kappa=0}^{a-1} (\bar{r}'_{i+\kappa} - \bar{r}'_{i+\kappa+1}) = \sum_{\kappa=0}^{a-1} [\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_{i+\kappa} \quad \forall \quad a \geq 1, \quad (115)$$

where we have used Eq. (113) in the last step. Thus we can write any of the $N(N-1)$ $\bar{r}'_i - \bar{r}'_j$ in terms of the $N-1$ $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$. That the $N-1$ $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$ form a minimal, irreducible, linearly independent set transforming under the $[N-1, 1]$ representation is assured since no linear combination of the $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$ can be formed to give $\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N]}$ of Eq. (184) in Paper I which transforms under the $[N]$ representation of S_N . Thus the $N-1$ $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$ lie in the $(N-1)$ -dimensional subspace orthogonal to the one-dimensional subspace of the $[N]$ sector, which as we have shown in Subsection 6.1, is the $[N-1, 1]$ irreducible carrier space of S_N . We have thus proved what we set out to prove, that the $N-1$ $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$ transform under the $[N-1, 1]$ irreducible representation of S_N .

As we have adverted in item a). of Sec. 7.1, the $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$ of Eq. (113) have the simplest functional form possible. Any other choice will involve linear combinations of the $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$ of Eq. (113) and will likely have a more complex functional form. At the very best they will involve another $(N-1)$ -dimensional subset of terms of the form $\bar{r}'_i - \bar{r}'_j$.

Furthermore, if we have two particles, we have only one primitive irreducible coordinate $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[1, 1]}]_1 = \bar{r}'_1 - \bar{r}'_2$. If we have three particles we have two primitive irreducible coordinates $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[2, 1]}]_1 = \bar{r}'_1 - \bar{r}'_2$ and $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[2, 1]}]_2 = \bar{r}'_2 - \bar{r}'_3$. Notice that adding one additional particle does not entail a change in the primitive irreducible coordinate, $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[2, 1]}]_1$, involving only the first two particles. Quite generally and by design, if we have $N-1$ particles and then add one more particle to the system, according to Eq. (113) the first primitive irreducible coordinates $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$, $1 \leq i \leq N-2$, involving the first $N-1$ particles only, are left unchanged by this addition. Thus we have

$$\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]} = \begin{pmatrix} \bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-2, 1]} \\ [\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_{N-1} \end{pmatrix}, \quad (116)$$

where $\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-2, 1]}$ is the primitive irreducible coordinate vector of the first $N-1$ particles, and $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_{N-1}$ is the primitive irreducible coordinate involving particles N and $N-1$.

From Eq. (54) we can identify $\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}$ as

$$[\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_{ij} = \delta_{i,j} - \delta_{i+1,j}, \quad \text{where } 1 \leq i \leq N-1 \text{ and } 1 \leq j \leq N. \quad (117)$$

In matrix form this is

$$\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]} = \begin{pmatrix} 1 & -1 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 1 & -1 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 1 & -1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 1 & -1 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 1 & -1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix}. \quad (118)$$

Notice that if we have $N-1$ particles and then add one more particle to the system, according to Eqs. (117) and (118), the first $N-2$ rows of the matrix $\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}$ are unchanged by the addition of an additional row, aside, that is, from the addition of an extra zero element at the end of the row, c.f. the discussion of the

paragraph prior to this one. To put it more succinctly we have

$$\overline{W}_{\vec{r}'}^{[N-1, 1]} = \left(\begin{array}{cccc|c} & & & & 0 \\ & & & & 0 \\ & & & & \vdots \\ & & & & 0 \\ \hline 0 & 0 & \dots & 0 & 1 \\ & & & & -1 \end{array} \right). \quad (119)$$

The Symmetry Coordinate To derive $W_{\vec{r}'}^{[N-1, 1]}$ and then the the symmetry coordinate $\mathbf{S}_{\vec{r}'}^{[N-1, 1]}$ via Eq. (73), we use Eq. (74) to calculate $U_{\vec{r}'}^{[N-1, 1]}$ and then Eq. (70) to arrive at $W_{\vec{r}'}^{[N-1, 1]}$. The first step in this process is to evaluate $\overline{W}_{\vec{r}'}^{[N-1, 1]} [\overline{W}_{\vec{r}'}^{[N-1, 1]}]^T$. From Eq. (117) we can readily show that

$$\left(\overline{W}_{\vec{r}'}^{[N-1, 1]} [\overline{W}_{\vec{r}'}^{[N-1, 1]}]^T \right)_{i,k} = \sum_{j=1}^N [\overline{W}_{\vec{r}'}^{[N-1, 1]}]_{i,j} [\overline{W}_{\vec{r}'}^{[N-1, 1]}]_{k,j} = -\delta_{i+1,k} + 2\delta_{i,k} - \delta_{i,k+1}, \quad (120)$$

which in matrix form is

$$\overline{W}_{\vec{r}'}^{[N-1, 1]} [\overline{W}_{\vec{r}'}^{[N-1, 1]}]^T = \begin{pmatrix} 2 & -1 & 0 & 0 & 0 & \dots \\ -1 & 2 & -1 & 0 & 0 & \dots \\ 0 & -1 & 2 & -1 & 0 & \dots \\ 0 & 0 & -1 & 2 & -1 & \dots \\ 0 & 0 & 0 & -1 & 2 & \ddots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix} = \begin{pmatrix} & & & & 0 \\ & & & & 0 \\ & & & & \vdots \\ & & & & 0 \\ \hline & & & & -1 \\ 0 & 0 & \dots & 0 & -1 \\ & & & & 2 \end{pmatrix}. \quad (121)$$

Now Eqs. (74) and (120) (or Eq. (121)) do not uniquely define $U_{\vec{r}'}^{[N-1, 1]}$ as we can transform $U_{\vec{r}'}^{[N-1, 1]}$ on the left by any orthogonal matrix, and the result will still satisfy Eq. (74). However, as we have noted above in item b). of Sec. 7.1., according to Eq. (64) the symmetry coordinates are composed of linear combinations of the primitive irreducible coordinates. Thus we choose the first symmetry coordinate to be proportional to just the first primitive irreducible coordinate, i.e.

$$[\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_1 \propto [\overline{\mathbf{S}}_{\vec{r}'}^{[N-1, 1]}]_1 = \vec{r}'_1 - \vec{r}'_2. \quad (122)$$

This involves only the first two particles in the simplest motion possible under the requirement that the symmetry coordinate transforms irreducibly under the $[N-1, 1]$ representation of S_N . If $N = 2$, $[\mathbf{S}_{\vec{r}'}^{[1, 1]}]_1$ is the sole symmetry coordinate transforming under the $[1, 1]$ representation of S_2 . For $N > 2$, we require the symmetry coordinate vector to satisfy

$$\mathbf{S}_{\vec{r}'}^{[N-1, 1]} = \begin{pmatrix} \mathbf{S}_{\vec{r}'}^{[N-1, 1]} \\ [\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_{N-1} \end{pmatrix}, \quad (123)$$

c.f. Eq. (116). Equations (122) and (123) mean that $[\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_i$ is formed from the first i elements of the $\overline{\mathbf{S}}_{\vec{r}'}$ vector, which means that it is formed from the first $i+1$ elements of the \vec{r}' vector, i.e. it involves the motion of only the first $i+1$ particles.

Thus from Eq. (70) we see that $U_{\vec{r}'}^{[N-1, 1]}$ is a lower triangular matrix, and if we further require all of its non-zero elements in the lower triangle to be positive, these requirements, together with Eq. (74), uniquely specify $U_{\vec{r}'}^{[N-1, 1]}$. Defining

$$\begin{aligned}\Theta_{\alpha-\beta} &= \sum_{m=1}^{\alpha-1} \delta_{m,\beta} \\ &= 1 \text{ when } \alpha - \beta > 0 \\ &= 0 \text{ when } \alpha - \beta \leq 0,\end{aligned}\tag{124}$$

and solving Eq. (74) for $U_{\vec{r}'}^{[N-1, 1]}$, subject to the above conditions, yields

$$[U_{\vec{r}'}^{[N-1, 1]}]_{ij} = \frac{j}{\sqrt{i(i+1)}} \sum_{m=1}^i \delta_{mj} = \frac{j}{\sqrt{i(i+1)}} \Theta_{i-j+1} \quad (125)$$

where

$$\begin{aligned}\Theta_{i-j+1} &= \sum_{m=1}^i \delta_{mj} = 1 \text{ when } j-i < 1 \\ &= 0 \text{ when } j-i \geq 1.\end{aligned}\tag{126}$$

In matrix form Eq. (125) reads

$$U_{\vec{r}'}^{[N-1, 1]} = \begin{pmatrix} \frac{1}{\sqrt{1}\sqrt{2}} & 0 & 0 & 0 & 0 & \cdots \\ \frac{1}{\sqrt{2}\sqrt{3}} & \frac{2}{\sqrt{2}\sqrt{3}} & 0 & 0 & 0 & \cdots \\ \frac{1}{\sqrt{3}\sqrt{4}} & \frac{2}{\sqrt{3}\sqrt{4}} & \frac{3}{\sqrt{3}\sqrt{4}} & 0 & 0 & \cdots \\ \frac{1}{\sqrt{4}\sqrt{5}} & \frac{2}{\sqrt{4}\sqrt{5}} & \frac{3}{\sqrt{4}\sqrt{5}} & \frac{4}{\sqrt{4}\sqrt{5}} & 0 & \cdots \\ \frac{1}{\sqrt{5}\sqrt{6}} & \frac{2}{\sqrt{5}\sqrt{6}} & \frac{3}{\sqrt{5}\sqrt{6}} & \frac{4}{\sqrt{5}\sqrt{6}} & \frac{5}{\sqrt{5}\sqrt{6}} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$= \left(\begin{array}{ccccc|c} & & & & & 0 \\ & & & & & 0 \\ & & & & & \vdots \\ & & & & & 0 \\ & & & & & 0 \\ U_{\vec{r}'}^{[N-2, 1]} & & & & & \\ \hline \frac{1}{\sqrt{N-1}\sqrt{N}} & \frac{2}{\sqrt{N-1}\sqrt{N}} & \cdots & \frac{N-3}{\sqrt{N-1}\sqrt{N}} & \frac{N-2}{\sqrt{N-1}\sqrt{N}} & \frac{N-1}{\sqrt{N-1}\sqrt{N}} \end{array} \right). \quad (127)$$

Thus from Eqs. (70), (117) and (125),

$$[W_{\mathbf{r}'}^{[N-1, 1]}]_{ik} = \frac{1}{\sqrt{i(i+1)}} \left(\sum_{m=1}^i \delta_{mk} - i\delta_{i+1,k} \right) = \frac{1}{\sqrt{i(i+1)}} (\Theta_{i-k+1} - i\delta_{i+1,k}) , \quad (128)$$

where $1 \leq i \leq N-1$ and $1 \leq k \leq N$. In matrix form this is

$$\begin{aligned}
W_{\vec{r}'}^{[N-1, 1]} &= \begin{pmatrix} \frac{1}{\sqrt{1\sqrt{2}}} & -\frac{1}{\sqrt{1\sqrt{2}}} & 0 & 0 & 0 & 0 & \cdots \\ \frac{1}{\sqrt{2\sqrt{3}}} & \frac{1}{\sqrt{2\sqrt{3}}} & -\frac{2}{\sqrt{2\sqrt{3}}} & 0 & 0 & 0 & \cdots \\ \frac{1}{\sqrt{3\sqrt{4}}} & \frac{1}{\sqrt{3\sqrt{4}}} & \frac{1}{\sqrt{3\sqrt{4}}} & -\frac{3}{\sqrt{3\sqrt{4}}} & 0 & 0 & \cdots \\ \frac{1}{\sqrt{4\sqrt{5}}} & \frac{1}{\sqrt{4\sqrt{5}}} & \frac{1}{\sqrt{4\sqrt{5}}} & \frac{1}{\sqrt{4\sqrt{5}}} & -\frac{4}{\sqrt{4\sqrt{5}}} & 0 & \cdots \\ \frac{1}{\sqrt{5\sqrt{6}}} & \frac{1}{\sqrt{5\sqrt{6}}} & \frac{1}{\sqrt{5\sqrt{6}}} & \frac{1}{\sqrt{5\sqrt{6}}} & \frac{1}{\sqrt{5\sqrt{6}}} & -\frac{5}{\sqrt{5\sqrt{6}}} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \\
&= \left(\begin{array}{c|c} & \begin{matrix} 0 \\ 0 \\ \vdots \\ 0 \end{matrix} \\ \hline W_{\vec{r}'}^{[N-2, 1]} & -\frac{N-1}{\sqrt{N-1}\sqrt{N}} \end{array} \right). \quad (129)
\end{aligned}$$

Thus the symmetry coordinate $\mathbf{S}_{\vec{r}'}^{[N-1, 1]}$ from Eqs. (73) and (128) is

$$[\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_i = \frac{1}{\sqrt{i(i+1)}} \left(\sum_{k=1}^i \bar{r}'_k - i\bar{r}'_{i+1} \right), \quad \text{where } 1 \leq i \leq N-1. \quad (130)$$

In matrix form this reads

$$\mathbf{S}_{\vec{r}'}^{[N-1, 1]} = \begin{pmatrix} \frac{1}{\sqrt{1\sqrt{2}}}(\bar{r}'_1 - \bar{r}'_2) \\ \frac{1}{\sqrt{2\sqrt{3}}}(\bar{r}'_1 + \bar{r}'_2 - 2\bar{r}'_3) \\ \frac{1}{\sqrt{3\sqrt{4}}}(\bar{r}'_1 + \bar{r}'_2 + \bar{r}'_3 - 3\bar{r}'_4) \\ \frac{1}{\sqrt{4\sqrt{5}}}(\bar{r}'_1 + \bar{r}'_2 + \bar{r}'_3 + \bar{r}'_4 - 4\bar{r}'_5) \\ \vdots \\ \frac{1}{\sqrt{N-1}\sqrt{N}} \left(\sum_{k=1}^{N-1} \bar{r}'_k - (N-1)\bar{r}'_N \right) \end{pmatrix} = \begin{pmatrix} \mathbf{S}_{\vec{r}'}^{[N-2, 1]} \\ [\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_{N-1} \end{pmatrix}, \quad (131)$$

where $\mathbf{S}_{\vec{r}'}^{[N-2, 1]}$ is the symmetry coordinate vector of the first $N-1$ particles and $[\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_{N-1}$ is the additional symmetry coordinate involving all N particles. We see from Eqs. (130) and (131) that the complexity of the motions described by the symmetry coordinates is kept to a minimum and builds up slowly as more particles become involved. Referring again to Eqs. (123) and (131), we again advert that adding another particle to the system does not cause widespread disruption to the symmetry coordinates. The symmetry coordinates, and the motions they describe, remain the same except for an additional symmetry coordinate which describes a motion involving all of the particles.

Motions Associated with Symmetry Coordinates $[\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_{\xi}$. According to Eqs. (78), (81), (79) and (128), the motions associated with symmetry coordinates $[\mathbf{S}_{\vec{r}'}^{[N-1, 1]}]_{\xi}$ in the unscaled internal displacement

coordinates \mathbf{r} about the unscaled Lewis structure configuration

$$\mathbf{r}_\infty = D^2 \bar{a}_{ho} \bar{\mathbf{r}}'_\infty \mathbf{1}_{\bar{\mathbf{r}}'} \quad (132)$$

are given by

$$\begin{aligned} (r_\xi^{[N-1, 1]})_i &= \bar{a}_{ho} D^{3/2} (r_\xi'^{[N-1, 1]})_i = \bar{a}_{ho} D^{3/2} [\mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_\xi [(W_{\bar{\mathbf{r}}'}^{[N-1, 1]})_\xi]_i \\ &= \bar{a}_{ho} \sqrt{\frac{D^3}{\xi(\xi+1)}} [\mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_\xi \left(\sum_{m=1}^{\xi} \delta_{mi} - \xi \delta_{\xi+1, i} \right) \\ &= \bar{a}_{ho} \sqrt{\frac{D^3}{\xi(\xi+1)}} [\mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_\xi (\Theta_{\xi-i+1} - \xi \delta_{\xi+1, i}) . \end{aligned} \quad (133)$$

Thus we see that the motion associated with symmetry coordinate $[\mathbf{S}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_1$ is an antisymmetric stretch motion about the Lewis structure configuration involving particles 1 and 2. As ξ gets larger, the motion involves more particles, $\xi + 1$ particles, where the first ξ particles move one way while the $(\xi + 1)^{\text{th}}$ moves in the other. Paradoxically though, as ξ increases the motion becomes more single-particle-like since the $(\xi + 1)^{\text{th}}$ radius vector in Eq. (133) is weighted by the quantity ξ .

8.1.2 The $\bar{\gamma}'$ Sector.

The Primitive Irreducible Coordinate. Again according to item a). above, $\bar{\mathbf{S}}_{\bar{\gamma}'}^{[N-1, 1]}$ should transform under exactly the same non-orthogonal irreducible $[N - 1, 1]$ representation of S_N as $\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}$. If $\hat{\mathbf{r}}_i$ is the unit vector from the center of the confining field to particle i , then $\hat{\mathbf{r}}_i - \widehat{\mathbf{r}}_{i+1}$, where $1 \leq i \leq N - 1$, transform under exactly the same $[N - 1, 1]$ irreducible representation of S_N as the primitive irreducible coordinate of the $\bar{\mathbf{r}}'$ sector, $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$, of Eq. (113). We also have that $\sum_{i=1}^N \hat{\mathbf{r}}_i$ is invariant under S_N , and so $(\hat{\mathbf{r}}_i - \widehat{\mathbf{r}}_{i+1}) \cdot (\sum_{j=1}^N \hat{\mathbf{r}}_j) = \sum_{j=1}^N (\hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_j - \widehat{\mathbf{r}}_{i+1} \cdot \hat{\mathbf{r}}_j)$ will transform under exactly the same $[N - 1, 1]$ irreducible representation of S_N as the primitive irreducible coordinate of the $\bar{\mathbf{r}}'$ sector, $[\bar{\mathbf{S}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_i$, of Eq. (113). Upon using

$$\gamma_{ij} = \hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_j , \quad (134)$$

this becomes $\sum_{j=1}^N (\gamma_{ij} - \gamma_{(i+1)j})$. Since $\gamma_{ii} = 1$, $\sum_{j=1}^N (\gamma_{ij} - \gamma_{(i+1)j}) = \sum_{j \neq i} \gamma_{ij} - \sum_{j \neq i+1} \gamma_{(i+1)j}$ and upon using Eq. (20) we obtain $\delta^{1/2} (\sum_{j \neq i} \bar{\gamma}'_{ij} - \sum_{j \neq i+1} \bar{\gamma}'_{(i+1)j})$. Thus we identify the primitive irreducible coordinate of the $[N - 1, 1]$ representation in the $\bar{\gamma}'$ sector as

$$[\bar{\mathbf{S}}_{\bar{\gamma}'}^{[N-1, 1]}]_i = \sum_{j \neq i} \bar{\gamma}'_{ij} - \sum_{j \neq i+1} \bar{\gamma}'_{(i+1)j} = \left(\sqrt[4]{D} \hat{\mathbf{r}}_i - \sqrt[4]{D} \widehat{\mathbf{r}}_{i+1} \right) \cdot \left(\sum_{j=1}^N \sqrt[4]{D} \hat{\mathbf{r}}_j \right) . \quad (135)$$

So what is $\bar{\mathbf{W}}_{\bar{\gamma}'}^{[N-1, 1]}$? From Eqs. (184) of Paper I, and Eqs. (73) and (113)

$$[\bar{\mathbf{S}}_{\bar{\gamma}'}^{[N-1, 1]}]_i = \sum_{k,l=1}^N [\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_{ik} [\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N]}]_{kl} \left(\sqrt[4]{D} \hat{\mathbf{r}}_k \right) \cdot \left(\sqrt[4]{D} \hat{\mathbf{r}}_l \right) = \sum_{k,l=1}^N [\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N-1, 1]}]_{ik} [\bar{\mathbf{W}}_{\bar{\mathbf{r}}'}^{[N]}]_{kl} \bar{\gamma}'_{kl} \quad (136)$$

and since $\overline{\gamma}'_{kl}$ is symmetric Eq. (136) may be recast as

$$[\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-1, 1]}]_i = \frac{1}{2} \sum_{k \neq l=1}^N \left([\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{ik} [\overline{W}_{\overline{\mathbf{r}}'}^{[N]}]_l + [\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{il} [\overline{W}_{\overline{\mathbf{r}}'}^{[N]}]_k \right) \overline{\gamma}'_{kl}. \quad (137)$$

Using Eqs. (185) of Paper I, and Eqs. (23) and (81) in Eq. (137) we have

$$[\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-1, 1]}]_i = \sum_{l=2}^N \sum_{k=1}^{l-1} \left([\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{ik} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + [\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{il} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k \right) \overline{\gamma}'_{kl}. \quad (138)$$

Thus we identify

$$[\overline{W}_{\overline{\gamma}'}^{[N-1, 1]}]_{i, kl} = \left([\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{ik} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + [\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{il} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k \right), \quad (139)$$

where $[\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{ik}$ and $[\mathbf{1}_{\overline{\mathbf{r}}'}]_l$ are given by Eqs. (117) (or Eq. (118)) and (81) respectively. Thus

$$[\overline{W}_{\overline{\gamma}'}^{[N-1, 1]}]_{i, kl} = \{ (\delta_{ik} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + \delta_{il} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k) - (\delta_{i+1, k} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + \delta_{i+1, l} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k) \}, \quad (140)$$

where $1 \leq k < l \leq N$ and $1 \leq i \leq N-1$.

The Symmetry Coordinate. To derive $W_{\overline{\gamma}'}^{[N-1, 1]}$ and then the symmetry coordinate $\mathcal{S}_{\overline{\gamma}'}^{[N-1, 1]}$ via Eq. (73), we use Eqs. (75), (76) and (125) to calculate $U_{\overline{\gamma}'}^{[N-1, 1]}$ and then Eq. (71) to arrive at $W_{\overline{\gamma}'}^{[N-1, 1]}$. The first step in this process is to evaluate $\overline{W}_{\overline{\gamma}'}^{[N-1, 1]} [\overline{W}_{\overline{\gamma}'}^{[N-1, 1]}]^T$. From Eq. (139) we derive

$$[\overline{W}_{\overline{\gamma}'}^{[N-1, 1]} [\overline{W}_{\overline{\gamma}'}^{[N-1, 1]}]^T]_{ij} = (N-2) [\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]} [\overline{W}_{\overline{\mathbf{r}}'}^{[N-1, 1]}]^T]_{ij} \quad (141)$$

and from Eqs. (75) and (76):

$$U_{\overline{\gamma}'}^{[N-1, 1]} = \frac{1}{\sqrt{N-2}} U_{\overline{\mathbf{r}}'}^{[N-1, 1]}, \quad (142)$$

where $U_{\overline{\mathbf{r}}'}^{[N-1, 1]}$ is given by Eqs. (125) (or Eq. (127)).

Thus from Eqs. (71), (139) and (142):

$$[W_{\overline{\gamma}'}^{[N-1, 1]}]_{i, kl} = \frac{1}{\sqrt{N-2}} \left([W_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{ik} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + [W_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{il} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k \right), \quad (143)$$

where $[W_{\overline{\mathbf{r}}'}^{[N-1, 1]}]_{ik}$ and $[\mathbf{1}_{\overline{\mathbf{r}}'}]_l$ are given by Eqs. (128) (or Eq. (129)) and (81) respectively. Upon using Eq. (128) in Eq. (143) we obtain

$$\begin{aligned} [W_{\overline{\gamma}'}^{[N-1, 1]}]_{i, kl} &= \\ &= \frac{1}{\sqrt{i(i+1)(N-2)}} \left(\sum_{m=1}^i (\delta_{mk} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + \delta_{ml} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k) - i(\delta_{i+1, k} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + \delta_{i+1, l} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k) \right) \\ &= \frac{1}{\sqrt{i(i+1)(N-2)}} \left((\Theta_{i-k+1} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + \Theta_{i-l+1} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k) - i(\delta_{i+1, k} [\mathbf{1}_{\overline{\mathbf{r}}'}]_l + \delta_{i+1, l} [\mathbf{1}_{\overline{\mathbf{r}}'}]_k) \right), \end{aligned} \quad (144)$$

where $1 \leq k < l \leq N$ and $1 \leq i \leq N-1$.

Using Eqs. (23) and (144) in Eq. (73), we obtain the symmetry coordinate

$$\begin{aligned}
[\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}]_i &= \frac{1}{\sqrt{i(i+1)(N-2)}} \left(\sum_{k=1}^i \sum_{l=1}^N \overline{\gamma}'_{kl} - i \sum_{l=1}^N \overline{\gamma}'_{i+1, l} \right) \\
&= \frac{1}{\sqrt{i(i+1)(N-2)}} \left(\sum_{k=1}^i \sum_{l \neq k=1}^N \overline{\gamma}'_{kl} - i \sum_{l \neq i+1=1}^N \overline{\gamma}'_{i+1, l} \right) \\
&= \frac{1}{\sqrt{i(i+1)(N-2)}} \left(\left[\sum_{l=2}^i \sum_{k=1}^{l-1} \overline{\gamma}'_{kl} + \sum_{k=1}^i \sum_{l=k+1}^N \overline{\gamma}'_{kl} \right] - i \left[\sum_{k=1}^i \overline{\gamma}'_{k, i+1} + \sum_{l=i+2}^N \overline{\gamma}'_{i+1, l} \right] \right).
\end{aligned} \tag{145}$$

Motions Associated with Symmetry Coordinate $\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}$. According to Eqs. (78), (80), (82) and (144), the motions associated with symmetry coordinates $[\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}]_\xi$ in the unscaled internal displacement coordinates γ about the unscaled Lewis structure configuration

$$\gamma_\infty = \gamma_\infty \mathbf{1}_{\overline{\gamma}'} \tag{146}$$

are given by

$$\begin{aligned}
(\gamma_\xi^{[N-1, 1]})_{ij} &= \frac{1}{\sqrt{D}} (\gamma'_\xi^{[N-1, 1]})_{ij} = \frac{1}{\sqrt{D}} [\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}]_\xi [(W_{\overline{\gamma}'}^{[N-1, 1]})_\xi]_{ij} \\
&= \frac{1}{\sqrt{\xi(\xi+1)(N-2)D}} [\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}]_\xi \left(\sum_{m=1}^\xi (\delta_{mi} [\mathbf{1}_{\overline{\gamma}'}]_{mj} + \delta_{mj} [\mathbf{1}_{\overline{\gamma}'}]_{mi}) - \xi (\delta_{\xi+1, i} [\mathbf{1}_{\overline{\gamma}'}]_{ij} + \delta_{\xi+1, j} [\mathbf{1}_{\overline{\gamma}'}]_{ij}) \right) \\
&= \frac{1}{\sqrt{\xi(\xi+1)(N-2)D}} [\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}]_\xi \left((\Theta_{\xi-i+1} [\mathbf{1}_{\overline{\gamma}'}]_{ij} + \Theta_{\xi-j+1} [\mathbf{1}_{\overline{\gamma}'}]_{ij}) - \xi (\delta_{\xi+1, i} [\mathbf{1}_{\overline{\gamma}'}]_{ij} + \delta_{\xi+1, j} [\mathbf{1}_{\overline{\gamma}'}]_{ij}) \right).
\end{aligned} \tag{147}$$

Thus we see that the motion associated with symmetry coordinate $[\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}]_1$ is an antisymmetric bending motion about the Lewis structure configuration where as the angle cosines $\gamma_{13}, \gamma_{14}, \gamma_{15}, \dots$ increase, $\gamma_{23}, \gamma_{24}, \gamma_{25}, \dots$ decrease and vice versa while $\gamma_{12}, \gamma_{34}, \gamma_{35}, \gamma_{45}, \dots$ remain unchanged. Thus as for the $\overline{\mathbf{r}}'$ sector of the $[N-1, 1]$ species, $[\mathbf{S}_{\overline{\gamma}'}^{[N-1, 1]}]_1$ involves the motions of particles 1 and 2 moving with opposite phase to each other against the remaining particles. As ξ gets larger, the motion involves more particles, $\xi+1$ particles, where the $(\xi+1)^{\text{th}}$ particle moves with opposite phase to the first ξ particles. Paradoxically though, and again like the $\overline{\mathbf{r}}'$ sector of the $[N-1, 1]$ species, as ξ increases the motion becomes more single-particle-like since the angle cosines involving the $(\xi+1)^{\text{th}}$ particle in Eq. (147) are weighted by the quantity ξ .

8.2 Symmetry Coordinates Belonging to the $[N-2, 2]$ Species.

There is only one sector, the $\overline{\gamma}'$ sector, belonging to the $[N-2, 2]$ species.

The Primitive Irreducible Coordinate. Consider the quantities

$$(\widehat{\mathbf{r}}_i - \widehat{\mathbf{r}}_j) \cdot (\widehat{\mathbf{r}}_k - \widehat{\mathbf{r}}_l) = \gamma_{ik} - \gamma_{il} + \gamma_{jl} - \gamma_{jk}, \quad \text{for } i \neq j \neq k \neq l \text{ and } j > i, l > k. \tag{148}$$

There are $N!/ [2^3(N-4)!]$ such elements[15] which transform into themselves under S_N . According to Eq. (20)

$$\gamma_{ik} - \gamma_{il} + \gamma_{jl} - \gamma_{jk} = \frac{1}{\sqrt{D}}(\overline{\gamma}'_{ik} - \overline{\gamma}'_{il} + \overline{\gamma}'_{jl} - \overline{\gamma}'_{jk}) \quad (149)$$

so that

$$\overline{\gamma}'_{ik} - \overline{\gamma}'_{il} + \overline{\gamma}'_{jl} - \overline{\gamma}'_{jk} = (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l), \quad \text{where } i \neq j \neq k \neq l \text{ and } j > i, l > k \quad (150)$$

and

$$\widehat{\mathbf{r}}'_i = \sqrt[4]{D} \widehat{\mathbf{r}}_i. \quad (151)$$

The $N!/ [2^3(N-4)!]$ $(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l)$ also transform into themselves under S_N . We wish to show that there are $N(N-3)/2$ linearly independent $(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l)$, a particular set of which we choose to be the primitive irreducible coordinates of the $[N-2, 2]$ species.

There are two distinct sets of linear dependencies relating the $N!/ [2^3(N-4)!]$ $(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l)$,

$$(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_m - \widehat{\mathbf{r}}'_l) + (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_m) = (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l) \quad \text{and} \quad (152)$$

$$(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_k) \cdot (\widehat{\mathbf{r}}'_j - \widehat{\mathbf{r}}'_l) + (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_l) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_j) = (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l). \quad (153)$$

The number $N!/ [2^3(N-4)!]$ is huge when N is large, but the linear dependencies of Eqs. (152) and (153) however, drastically reduce the number to $N(N-3)/2$ linearly independent terms.

Through Eq. (152) we can write

$$(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_j) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l) = \sum_{\kappa=0}^{j-i-1} (\widehat{\mathbf{r}}'_{i+\kappa} - \widehat{\mathbf{r}}'_{i+1+\kappa}) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l). \quad (154)$$

Thus we only need to consider the $(N-1)(N-2)(N-3)/2$ $(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l)$, where $i \neq j \neq k \neq l$ and $l > k$.

Equation (152) may be used iteratively again to reduce the number of $(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l)$ by writing

$$(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l) = \sum_{\zeta=0}^{l-k-1} (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_{k+\zeta} - \widehat{\mathbf{r}}'_{k+1+\zeta}) \quad \text{when } l < i \text{ or } k > i+1, \quad (155)$$

and

$$\begin{aligned} & (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_k - \widehat{\mathbf{r}}'_l) = \\ & = \sum_{\zeta=0}^{l-i-3} (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_{k+\zeta} - \widehat{\mathbf{r}}'_{k+1+\zeta}) + (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_{l-1} - \widehat{\mathbf{r}}'_{i+2}) + \\ & + \sum_{\zeta=0}^{l-i-3} (\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_{i+2+\zeta} - \widehat{\mathbf{r}}'_{i+3+\zeta}) \quad \text{when } k < i \text{ and } l > i+1. \end{aligned} \quad (156)$$

Thus we only need to consider the $(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_{l-1} - \widehat{\mathbf{r}}'_l)$ where $2 \leq l \leq i-1$ or $i+3 \leq l \leq N$ and $1 \leq i \leq N-1$, and $(\widehat{\mathbf{r}}'_i - \widehat{\mathbf{r}}'_{i+1}) \cdot (\widehat{\mathbf{r}}'_{i-1} - \widehat{\mathbf{r}}'_{i+2})$, where $1 \leq i \leq N-1$, i.e. $(N-1)(N-3)$ elements to consider.

Now let's apply Eq. (153) to this reduced subset. Consider the case where $2 \leq l \leq i-1$. In this case Eq. (153) yields the unsurprising result

$$\begin{aligned}
(\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_{l-1}' - \widehat{\mathbf{r}}_l') &= (\widehat{\mathbf{r}}_{l-1}' - \widehat{\mathbf{r}}_i') \cdot (\widehat{\mathbf{r}}_l' - \widehat{\mathbf{r}}_{i+1}') - (\widehat{\mathbf{r}}_l' - \widehat{\mathbf{r}}_i') \cdot (\widehat{\mathbf{r}}_{l-1}' - \widehat{\mathbf{r}}_{i+1}') = \\
&= (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{l-1}') \cdot (\widehat{\mathbf{r}}_{i+1}' - \widehat{\mathbf{r}}_l') - (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_l') \cdot (\widehat{\mathbf{r}}_{i+1}' - \widehat{\mathbf{r}}_{l-1}') = \\
&= (\widehat{\mathbf{r}}_{l-1}' - \widehat{\mathbf{r}}_l') \cdot (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}'),
\end{aligned} \tag{157}$$

i.e. we can write all of the $(\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_{l-1}' - \widehat{\mathbf{r}}_l')$ where $2 \leq l \leq i-1$ and $3 \leq i \leq N-1$ in terms of the $(\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_{l-1}' - \widehat{\mathbf{r}}_l')$ with $i+3 \leq l \leq N$ and $1 \leq i \leq N-3$.

Thus we reduce our $N!/2^3(N-4)!$ elements of the form $(\widehat{\mathbf{r}}_i - \widehat{\mathbf{r}}_j) \cdot (\widehat{\mathbf{r}}_k - \widehat{\mathbf{r}}_l)$, where $i \neq j \neq k \neq l$, $j > i$ and $l > k$, down to the $(N-2)(N-3)/2$ elements $(\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_{l-1}' - \widehat{\mathbf{r}}_l')$ with $i+3 \leq l \leq N$ and $1 \leq i \leq N-3$, and the $N-3$ elements of the form $(\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_{i-1}' - \widehat{\mathbf{r}}_{i+2}')$, where $2 \leq i \leq N-2$. Hence we have $N(N-3)/2$ linearly elements, which is exactly the dimensionality of the $[N-2, 2]$ representation. We identify these elements as the primitive irreducible coordinates of the $[N-2, 2]$ representation and write

$$\overline{\mathbf{S}}_{\overline{\gamma}'}^{[N-2, 2]} = \begin{pmatrix} (\widehat{\mathbf{r}}_1' - \widehat{\mathbf{r}}_2') \cdot (\widehat{\mathbf{r}}_3' - \widehat{\mathbf{r}}_4') \\ (\widehat{\mathbf{r}}_2' - \widehat{\mathbf{r}}_3') \cdot (\widehat{\mathbf{r}}_1' - \widehat{\mathbf{r}}_4') \\ \hline (\widehat{\mathbf{r}}_1' - \widehat{\mathbf{r}}_2') \cdot (\widehat{\mathbf{r}}_4' - \widehat{\mathbf{r}}_5') \\ (\widehat{\mathbf{r}}_2' - \widehat{\mathbf{r}}_3') \cdot (\widehat{\mathbf{r}}_4' - \widehat{\mathbf{r}}_5') \\ (\widehat{\mathbf{r}}_3' - \widehat{\mathbf{r}}_4') \cdot (\widehat{\mathbf{r}}_2' - \widehat{\mathbf{r}}_5') \\ \hline (\widehat{\mathbf{r}}_1' - \widehat{\mathbf{r}}_2') \cdot (\widehat{\mathbf{r}}_5' - \widehat{\mathbf{r}}_6') \\ (\widehat{\mathbf{r}}_2' - \widehat{\mathbf{r}}_3') \cdot (\widehat{\mathbf{r}}_5' - \widehat{\mathbf{r}}_6') \\ (\widehat{\mathbf{r}}_3' - \widehat{\mathbf{r}}_4') \cdot (\widehat{\mathbf{r}}_5' - \widehat{\mathbf{r}}_6') \\ (\widehat{\mathbf{r}}_4' - \widehat{\mathbf{r}}_5') \cdot (\widehat{\mathbf{r}}_3' - \widehat{\mathbf{r}}_6') \\ \hline (\widehat{\mathbf{r}}_1' - \widehat{\mathbf{r}}_2') \cdot (\widehat{\mathbf{r}}_6' - \widehat{\mathbf{r}}_7') \\ (\widehat{\mathbf{r}}_2' - \widehat{\mathbf{r}}_3') \cdot (\widehat{\mathbf{r}}_6' - \widehat{\mathbf{r}}_7') \\ (\widehat{\mathbf{r}}_3' - \widehat{\mathbf{r}}_4') \cdot (\widehat{\mathbf{r}}_6' - \widehat{\mathbf{r}}_7') \\ (\widehat{\mathbf{r}}_4' - \widehat{\mathbf{r}}_5') \cdot (\widehat{\mathbf{r}}_6' - \widehat{\mathbf{r}}_7') \\ (\widehat{\mathbf{r}}_5' - \widehat{\mathbf{r}}_6') \cdot (\widehat{\mathbf{r}}_4' - \widehat{\mathbf{r}}_7') \\ \hline (\widehat{\mathbf{r}}_1' - \widehat{\mathbf{r}}_2') \cdot (\widehat{\mathbf{r}}_7' - \widehat{\mathbf{r}}_8') \\ \vdots \qquad \qquad \qquad \vdots \end{pmatrix}, \tag{158}$$

or

$$\begin{aligned}
[\overline{\mathbf{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} &= (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_{j-1}' - \widehat{\mathbf{r}}_j') \quad \text{when } i+3 \leq j \leq N \text{ and } 1 \leq i \leq N-3 \\
&= (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_{j-3}' - \widehat{\mathbf{r}}_j') \quad \text{when } j = i+2 \text{ and } 2 \leq i \leq N-2.
\end{aligned} \tag{159}$$

There are a myriad of ways to choose a set of $N(N-3)/2$ linearly independent, primitive irreducible coordinates from the $N!/2^3(N-4)!$ $(\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_j') \cdot (\widehat{\mathbf{r}}_k' - \widehat{\mathbf{r}}_l')$. However, the set we have chosen has some significant advantages as we shall see below.

What about $\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}$? From Eqs. (134), (159) and (160) we can write

$$[\overline{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} = \sum_{m=1}^N \sum_{n=1}^N (\delta_{im} - \delta_{i+1, m})(\delta_{kn} - \delta_{jn}) \widehat{\mathbf{r}}_m' \cdot \widehat{\mathbf{r}}_n' = \sum_{m=1}^N \sum_{n=1}^N (\delta_{im} - \delta_{i+1, m})(\delta_{kn} - \delta_{jn}) \overline{\gamma}'_{mn}, \quad (161)$$

where $k = j - 1$ when $i + 3 \leq j \leq N$ and $1 \leq i \leq N - 3$, or $k = j - 3$ when $j = i + 2$ and $2 \leq i \leq N - 2$.

Since $\overline{\gamma}'_{mn}$ is a symmetric matrix, Eq. (161) can be rewritten as

$$[\overline{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} = \sum_{n=2}^N \sum_{m=1}^{n-1} [(\delta_{im} - \delta_{i+1, m})(\delta_{kn} - \delta_{jn}) + (\delta_{in} - \delta_{i+1, n})(\delta_{km} - \delta_{jm})] \overline{\gamma}'_{mn}, \quad (162)$$

where $k = j - 1$ when $i + 3 \leq j \leq N$ and $1 \leq i \leq N - 3$, or $k = j - 3$ when $j = i + 2$ and $2 \leq i \leq N - 2$.

Thus from Eq. (73), we note that

$$W_{\overline{\gamma}'}^{\alpha} \overline{\gamma}' = \sum_{j=1}^N \sum_{i < j} [W_{\overline{\gamma}'}^{\alpha}]_{ij} \overline{\gamma}'_{ij}, \quad (163)$$

and Eq. (162) $\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}$ may be identified as

$$[\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, mn} = (\delta_{im} - \delta_{i+1, m})(\delta_{kn} - \delta_{jn}) + (\delta_{in} - \delta_{i+1, n})(\delta_{km} - \delta_{jm}), \quad (164)$$

where $2 \leq n \leq N$ and $1 \leq m \leq n - 1$, $k = j - 1$ when $i + 3 \leq j \leq N$ and $1 \leq i \leq N - 3$, or $k = j - 3$ when $j = i + 2$ and $2 \leq i \leq N - 2$. Equation (164) and the above conditions on k can be written as

$$\begin{aligned} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, mn} = & (\delta_{im} - \delta_{i+1, m}) \left((1 - \delta_{i, j-2}) \delta_{j-1, n} + \delta_{i, j-2} \delta_{j-3, n} - \delta_{jn} \right) \\ & + (\delta_{in} - \delta_{i+1, n}) \left((1 - \delta_{i, j-2}) \delta_{j-1, m} + \delta_{i, j-2} \delta_{j-3, m} - \delta_{jm} \right), \end{aligned} \quad (165)$$

where $1 \leq i \leq j - 2$, $i + 2 \leq j \leq N$, $2 \leq n \leq N$ and $1 \leq m \leq n - 1$.

The Symmetry Coordinate. We derive the symmetry coordinate $\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}$ from Eq. (64), via Eq. (74) to calculate $U_{\overline{\gamma}'}^{[N-2, 2]}$, and Eqs. (159) and (160) for $\overline{S}_{\overline{\gamma}'}^{[N-2, 2]}$. The first step in this process is to evaluate $\overline{W}_{\overline{\gamma}'}^{[N-2, 2]} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}]^T$. Using Eq. (164) we derive

$$\begin{aligned} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}]^T]_{ij, i'j'} &= \sum_{n=2}^N \sum_{m=1}^{n-1} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, mn} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}]_{i'j', mn} \\ &= \sum_{n=2}^N \sum_{m=1}^{n-1} [(\delta_{im} - \delta_{i+1, m})(\delta_{kn} - \delta_{jn}) + (\delta_{in} - \delta_{i+1, n})(\delta_{km} - \delta_{jm})] \times \\ &\quad \times [(\delta_{i'm} - \delta_{i'+1, m})(\delta_{k'n} - \delta_{j'n}) + (\delta_{i'n} - \delta_{i'+1, n})(\delta_{k'm} - \delta_{j'm})] \\ &= \sum_{n=1}^N \sum_{m=1}^N (\delta_{im} - \delta_{i+1, m})(\delta_{kn} - \delta_{jn}) \times \\ &\quad \times [(\delta_{i'm} - \delta_{i'+1, m})(\delta_{k'n} - \delta_{j'n}) + (\delta_{i'n} - \delta_{i'+1, n})(\delta_{k'm} - \delta_{j'm})], \end{aligned} \quad (166)$$

where the $m = n$ contribution is zero since $i \neq i + 1 \neq k \neq j$ and $i' \neq i' + 1 \neq k' \neq j'$. Thus

$$\begin{aligned} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]} [\overline{W}_{\overline{\gamma}'}^{[N-2, 2]}]^T]_{ij, i'j'} &= (\delta_{ii'} - \delta_{i, i'+1} - \delta_{i+1, i'} + \delta_{i+1, i'+1})(\delta_{kk'} - \delta_{kj'} - \delta_{jk'} + \delta_{jj'}) + \\ &\quad + (\delta_{ik'} - \delta_{ij'} - \delta_{i+1, k'} + \delta_{i+1, j'})(\delta_{ki'} - \delta_{k, i'+1} - \delta_{j i'} + \delta_{j, i'+1}) \\ &= R_{i(i+1)kj, i'(i'+1)k'j'} + R_{i(i+1)kj, k'j'i'(i'+1)}, \end{aligned} \quad (167)$$

where

$$R_{abcd, a'b'c'd'} = (\delta_{aa'} - \delta_{ab'} - \delta_{ba'} + \delta_{bb'}) (\delta_{cc'} - \delta_{cd'} - \delta_{dc'} + \delta_{dd'}), \quad (168)$$

$k = j - 1$ when $i + 3 \leq j \leq N$ and $1 \leq i \leq N - 3$, or $k = j - 3$ when $j = i + 2$ and $2 \leq i \leq N - 2$. Likewise, $k' = j' - 1$ when $i' + 3 \leq j' \leq N$ and $1 \leq i' \leq N - 3$, or $k' = j' - 3$ when $j' = i' + 2$ and $2 \leq i' \leq N - 2$.

We will find $U_{\vec{\gamma}}^{[N-2, 2]}$ of Eqs. (71) and (74) in a two step process. First of all we will introduce a transformation $\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}$ which block diagonalizes Eq. (167) in the j and j' indices. Subsequently we will then introduce a further transformation $\mathcal{I}_{\vec{\gamma}}^{[N-2, 2]}$ which diagonalizes the j blocks in the indices i and i' to yield Eq. (74). Thus we have that

$$U_{\vec{\gamma}}^{[N-2, 2]} = \mathcal{I}_{\vec{\gamma}}^{[N-2, 2]} \mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}. \quad (169)$$

Let's work with the transformation $\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}$ first. If we take $\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}$ to be

$$[\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}]_{ij, i'j'} = [\mathbf{1}_{\vec{r}'}]_j \delta_{i+1, j'} (1 - \delta_{i-1, i'}) i' + \delta_{ii'} \Theta_{j-j'+1} \Theta_{j'-i-1} (j' - 3), \quad (170)$$

then after some calculation we find

$$\begin{aligned} & \left[\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]} \overline{W}_{\vec{\gamma}}^{[N-2, 2]} [\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]} \overline{W}_{\vec{\gamma}}^{[N-2, 2]}]^T \right]_{ij, i'j'} = \\ &= \sum_{l=4}^N \sum_{k=1}^{l-2} \sum_{l'=4}^N \sum_{k'=1}^{l'-2} [\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}]_{ij, kl} \left[\overline{W}_{\vec{\gamma}}^{[N-2, 2]} \overline{W}_{\vec{\gamma}}^{[N-2, 2]} \right]_{kl, k'l'}^T [\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}]_{i'j', k'l'} \\ &= (2\delta_{ii'} - \delta_{i, i'+1} - \delta_{i+1, i'}) (j-3)(j-2) \delta_{jj'} \end{aligned} \quad (171)$$

Thus the transformation $\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}$ has block diagonalized Eq. (167) in the j and j' indices as advertised.

To understand what the transformation $\mathcal{J}_{\vec{\gamma}}^{[N-2, 2]}$ actually achieves, let's apply it to the primitive irre-

ducible coordinate $\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}$. Defining

$$\begin{aligned}
[\mathcal{T}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} &= [\mathcal{J}_{\overline{\gamma}'}^{[N-2, 2]} \overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} \\
&= \sum_{j'=4}^N \sum_{i'=1}^{j'-2} [\mathcal{J}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, i'j'} [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{i'j'} \\
&= \sum_{j'=4}^N \sum_{i'=1}^{j'-2} \left[\mathbf{1}_{\overline{\gamma}'}]_j \delta_{i+1, j'} (1 - \delta_{i-1, i'}) i' + \delta_{ii'} \Theta_{j-j'+1} \Theta_{j'-i-1} (j' - 3) \right] [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{i'j'} \\
&= \sum_{j'=4}^N \sum_{i'=1}^{j'-2} [\mathbf{1}_{\overline{\gamma}'}]_j \delta_{i+1, j'} (1 - \delta_{i-1, i'}) i' [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{i'j'} + \\
&\quad + \sum_{j'=4}^N \sum_{i'=1}^{j'-2} \delta_{ii'} \Theta_{j-j'+1} \Theta_{j'-i-1} (j' - 3) [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{i'j'} \\
&= \sum_{i'=1}^{i-2} i' [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{i', i+1} + \sum_{j'=i+2}^j (j' - 3) [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij'} \\
&= \sum_{i'=1}^{i-2} i' [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{i', i+1} + (i - 1) [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{i, i+2} + \sum_{j'=i+3}^j (j' - 3) [\overline{\mathcal{S}}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij'} \\
&= (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_1' + \widehat{\mathbf{r}}_2' + \widehat{\mathbf{r}}_3' + \cdots + \widehat{\mathbf{r}}_{i-1}' + \widehat{\mathbf{r}}_{i+2}' + \widehat{\mathbf{r}}_{i+3}' + \cdots + \widehat{\mathbf{r}}_{j-1}' - (j - 3) \widehat{\mathbf{r}}_j') \\
&= (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot \left(\sum_{j'=1}^{j-1} \widehat{\mathbf{r}}_{j'}' - (j - 3) \widehat{\mathbf{r}}_j' - (\widehat{\mathbf{r}}_i' + \widehat{\mathbf{r}}_{i+1}') \right), \tag{172}
\end{aligned}$$

where $\mathbf{1}_{\overline{\gamma}'}$ is defined in Eq. (81), Θ_{i-j} is defined in Eq. (124), and Eqs (159) and (160) have been used in the last step. The last term in parenthesis in the last line of Eq. (172) should be compared with Eq. (130). Not surprisingly, it has the same form as Eq. (130), except that it includes $N - 2$ particles, the i^{th} and $(i + 1)^{\text{th}}$ particles are not included. We further note that since

$$(\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot (\widehat{\mathbf{r}}_i' + \widehat{\mathbf{r}}_{i+1}') = 0, \tag{173}$$

$$[\mathcal{T}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} = (\widehat{\mathbf{r}}_i' - \widehat{\mathbf{r}}_{i+1}') \cdot \left(\sum_{j'=1}^{j-1} \widehat{\mathbf{r}}_{j'}' - (j - 3) \widehat{\mathbf{r}}_j' \right). \tag{174}$$

Looking now at each j block in Eq. (171), it is tridiagonal in the i index and has exactly the same form as Eq. (121), aside from the $(j - 3)(j - 2)$ multiplier. From Eq. (125) we see that $\mathcal{T}_{\overline{\gamma}'}^{[N-2, 2]}$ is

$$\begin{aligned}
[\mathcal{T}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, i'j'} &= \frac{1}{\sqrt{(j - 3)(j - 2)}} [U_{\overline{\gamma}'}^{[j-2, 1]}]_{ii'} \delta_{jj'} = \frac{i'}{\sqrt{i(i + 1)(j - 3)(j - 2)}} \sum_{m=1}^i \delta_{mi'} \delta_{jj'} \\
&= \frac{i'}{\sqrt{i(i + 1)(j - 3)(j - 2)}} \Theta_{i-i'+1} \delta_{jj'}, \tag{175}
\end{aligned}$$

where Θ_{i-j} is defined in Eq. (124). Thus from Eqs. (169), (170) and (175),

$$\begin{aligned}
& [U_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, i'j'} \\
&= \sum_{l=4}^N \sum_{k=1}^{l-2} [\mathcal{I}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, kl} [\mathcal{J}_{\overline{\gamma}'}^{[N-2, 2]}]_{kl, i'j'} \\
&= \sum_{k=1}^{j-2} \frac{1}{\sqrt{(j-3)(j-2)}} [U_{\overline{\mathbf{r}}'}^{[j-2, 1]}]_{ik} [\mathcal{J}_{\overline{\gamma}'}^{[N-2, 2]}]_{kj, i'j'} \\
&= \sum_{k=1}^{j-2} \frac{k}{\sqrt{i(i+1)(j-3)(j-2)}} \Theta_{i-k+1} \left([\mathbf{1}_{\overline{\mathbf{r}}'}]_j \delta_{k+1, j'} (1 - \delta_{k-1, i'}) i' + \delta_{ki'} \Theta_{j-j'+1} \Theta_{j'-k-1} (j' - 3) \right) \\
&= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left([\mathbf{1}_{\overline{\mathbf{r}}'}]_j i' (j' - 1) (1 - \delta_{i', j'-2}) \Theta_{i-j'+2} + i' (j' - 3) \Theta_{i-i'+1} \Theta_{j-j'+1} \Theta_{j'-i'-1} \right) \\
&= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left([\mathbf{1}_{\overline{\mathbf{r}}'}]_j i' (j' - 1) (1 - \delta_{i', j'-2}) \Theta_{i-j'+2} + i' (j' - 3) \Theta_{i-i'+1} \Theta_{j-j'+1} \right).
\end{aligned} \tag{176}$$

The symmetry coordinate $\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}$ is thus

$$[\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} = \sum_{l=4}^N \sum_{k=1}^{l-2} [\mathcal{I}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij, kl} [\mathbf{T}_{\overline{\gamma}'}^{[N-2, 2]}]_{kl}, \tag{177}$$

which from Eqs. (174) and (175) is

$$[\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{ij} = \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left(\sum_{k=1}^i \widehat{\mathbf{r}}_k' - i \widehat{\mathbf{r}}_{i+1}' \right) \cdot \left(\sum_{j'=1}^{j-1} \widehat{\mathbf{r}}_{j'}' - (j-3) \widehat{\mathbf{r}}_j' \right), \tag{178}$$

where $1 \leq i \leq j-2$ and $i+2 \leq j \leq N$. In matrix form $\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}$ may be written

$$\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]} = \begin{pmatrix} [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{14} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{24} \\ \hline [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{15} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{25} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{35} \\ \hline [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{16} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{26} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{36} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{46} \\ \hline [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{17} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{27} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{37} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{47} \\ [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{57} \\ \hline [\mathbf{S}_{\overline{\gamma}'}^{[N-2, 2]}]_{18} \\ \vdots \end{pmatrix}. \tag{179}$$

Motions Associated with Symmetry Coordinate $S_{\bar{\gamma}'}^{[N-2, 2]}$. To calculate the motions of the unscaled internal displacement coordinates γ about the unscaled Lewis structure configuration γ_∞ of Eq. (146) engendered by the symmetry coordinates $[S_{\bar{\gamma}'}^{[N-2, 2]}]_{ij}$, we use Eqs. (78), (80), (82) and (144). The first step in this process is the evaluation of $[W_{\bar{\gamma}'}^{[N-2, 2]}]_{ij, mn}$. From Eqs. (71), (165) and (176) we find that

$$\begin{aligned}
[W_{\bar{\gamma}'}^{[N-2, 2]}]_{ij, mn} &= \sum_{j'=4}^N \sum_{i'=1}^{j'-2} [U_{\bar{\gamma}'}^{[N-2, 2]}]_{ij, i'j'} [\bar{W}_{\bar{\gamma}'}^{[N-2, 2]}]_{i'j', mn} \\
&= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \sum_{j'=4}^N \sum_{i'=1}^{j'-2} \left([1_{\bar{r}'}]_j i'(j'-1)(1-\delta_{i', j'-2}) \Theta_{i-j'+2} + \right. \\
&\quad \left. + i'(j'-3) \Theta_{i-i'+1} \Theta_{j-j'+1} \right) \times \\
&\quad \times \left[(\delta_{i'm} - \delta_{i'+1, m}) \left((1-\delta_{i', j'-2}) \delta_{j'-1, n} + \delta_{i', j'-2} \delta_{j'-3, n} - \delta_{j'n} \right) + \right. \\
&\quad \left. + (\delta_{i'n} - \delta_{i'+1, n}) \left((1-\delta_{i', j'-2}) \delta_{j'-1, m} + \delta_{i', j'-2} \delta_{j'-3, m} - \delta_{j'm} \right) \right] \\
&= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left((\Theta_{i-m+1} - i\delta_{i+1, m})(\Theta_{j-n} - (j-3)\delta_{jn}) + \right. \\
&\quad \left. + (\Theta_{i-n+1} - i\delta_{i+1, n})(\Theta_{j-m} - (j-3)\delta_{jm}) \right), \tag{180}
\end{aligned}$$

c.f. Eq. (178). Thus

$$\begin{aligned}
(\gamma_{ij}^{[N-2, 2]})_{mn} &= \frac{1}{\sqrt{D}} (\gamma'_{ij}^{[N-2, 2]})_{mn} = \frac{1}{\sqrt{D}} [S_{\bar{\gamma}'}^{[N-2, 2]}]_{ij} [W_{\bar{\gamma}'}^{[N-2, 2]}]_{ij, mn} \\
&= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)D}} [S_{\bar{\gamma}'}^{[N-2, 2]}]_{ij} \left((\Theta_{i-m+1} - i\delta_{i+1, m})(\Theta_{j-n} - (j-3)\delta_{jn}) + \right. \\
&\quad \left. + (\Theta_{i-n+1} - i\delta_{i+1, n})(\Theta_{j-m} - (j-3)\delta_{jm}) \right), \tag{181}
\end{aligned}$$

where $1 \leq m < n \leq N$, and $1 \leq i \leq j-2$ and $i+2 \leq j \leq N$.

9 The Frequencies and Normal-Mode Coordinates of the System.

9.1 The G and FG matrices in the Symmetry-Coordinate Basis.

We can use the $W_{\bar{X}}^\alpha$ matrices of Eqs. (128), (144) and (180) to calculate the reduced G and FG matrix elements, $[\sigma_\alpha^G]_{X'_1, X'_2}$ and $[\sigma_\alpha^{FG}]_{X'_1, X'_2}$, of Eq. (85) for the $\alpha = [N-1, 1]$ and $[N-2, 2]$ species. The reduced matrix elements, $[\sigma_{[N]}^G]_{X'_1, X'_2}$ and $[\sigma_{[N]}^{FG}]_{X'_1, X'_2}$ for the $[N]$ sector are calculated in Paper I. An outline of this calculation is to be found in Appendix A, with the following results.

9.1.1 The $[N-1, 1]$ Species.

The Matrix Elements $[\sigma_{[N-1, 1]}^G]_{X'_1, X'_2}$. Using Eqs. (39), (40), (41), (42), (43), (46), (47), (48), (85), (128) and (144) we derive

$$\sigma_{[N-1, 1]}^G = \begin{pmatrix} [\sigma_{[N-1, 1]}^G]_{\bar{r}', \bar{r}'} = \tilde{a}' & [\sigma_{[N-1, 1]}^G]_{\bar{r}', \bar{\gamma}'} = 0 \\ [\sigma_{[N-1, 1]}^G]_{\bar{\gamma}', \bar{r}'} = 0 & [\sigma_{[N-1, 1]}^G]_{\bar{\gamma}', \bar{\gamma}'} = (\tilde{g}' + (N-2)\tilde{h}') \end{pmatrix}. \tag{182}$$

The Matrix Elements $[\sigma_{[N-1, 1]}^{FG}]_{\mathbf{x}'_1, \mathbf{x}'_2}$. Using Eqs. (39), (40), (41), (42), (43), (44), (45), (85), (99), (128) and (144) we derive

$$\sigma_{[N-1, 1]}^{FG} = \begin{pmatrix} [\sigma_{[N-1, 1]}^{FG}]_{\bar{\mathbf{r}}', \bar{\mathbf{r}}' = \tilde{a}} & [\sigma_{[N-1, 1]}^{FG}]_{\bar{\mathbf{r}}', \bar{\mathbf{r}}' = \sqrt{N-2} \tilde{e}} \\ [\sigma_{[N-1, 1]}^{FG}]_{\bar{\mathbf{r}}', \bar{\mathbf{r}}' = \sqrt{N-2} \tilde{e}} & [\sigma_{[N-1, 1]}^{FG}]_{\bar{\mathbf{r}}', \bar{\mathbf{r}}' = (\tilde{g} + (N-2)\tilde{h})} \end{pmatrix}. \quad (183)$$

9.1.2 The $[N-2, 2]$ Species.

The Matrix Element $[\sigma_{[N-2, 2]}^G]$. Using Eqs. (43), (46), (47), (48), (85) and (180) we derive

$$\sigma_{[N-2, 2]}^G = [\sigma_{[N-2, 2]}^G]_{\bar{\mathbf{r}}', \bar{\mathbf{r}}' = \tilde{g}'}. \quad (184)$$

The Matrix Element $[\sigma_{[N-2, 2]}^{FG}]$. Using Eqs. (43), (44), (45), (85) and (180) we derive

$$\sigma_{[N-2, 2]}^{FG} = [\sigma_{[N-2, 2]}^{FG}]_{\bar{\mathbf{r}}', \bar{\mathbf{r}}' = \tilde{g}'}. \quad (185)$$

9.2 The Frequencies and Normal Modes.

Using Eq. (183) in Eq. (101) we obtain $\lambda_{[N-1, 1]}^\pm$ and from Eqs. (185) and (96) we obtain $\lambda_{[N-2, 2]}$. The frequencies are then determined from Eq. (34). The $\lambda_{[N]}^\pm$ for the $[N]$ species are discussed in Paper I.

Likewise the normal modes $\mathbf{q}'_+^{[N]}$ and $\mathbf{q}'_-^{[N]}$ for the $[N]$ species are also calculated in Paper I (Eqs. (203) and (204)). In regards to the $[N-1, 1]$ species, the $\bar{\mathbf{r}}'$ - $\bar{\mathbf{r}}'$ mixing angles, $\theta_\pm^{[N-1, 1]}$, are determined from Eq. (102). The normalization constant $c^{[N-1, 1]}$ of the reduced normal-coordinate coefficient vector, $\mathbf{c}^{[N-1, 1]}$, of Eqs. (90) and (93) is determined from Eqs. (105) and (106). One then determines the normal mode vector, \mathbf{q}' , through Eqs. (107), (130), (145) and (178). Thus we arrive at

$$\begin{aligned} [\mathbf{q}'_+^{[N-1, 1]}]_i &= c_+^{[N-1, 1]} \cos \theta_+^{[N-1, 1]} \frac{1}{\sqrt{i(i+1)}} \left(\sum_{i=1}^i \bar{r}'_i - i \bar{r}'_{i+1} \right) \\ &+ c_+^{[N-1, 1]} \sin \theta_+^{[N-1, 1]} \frac{1}{\sqrt{i(i+1)(N-2)}} \left(\left[\sum_{l=2}^i \sum_{k=1}^{l-1} \bar{\gamma}'_{kl} + \sum_{k=1}^i \sum_{l=k+1}^N \bar{\gamma}'_{kl} \right] \right. \\ &\quad \left. - i \left[\sum_{k=1}^i \bar{\gamma}'_{k, i+1} + \sum_{l=i+2}^N \bar{\gamma}'_{i+1, l} \right] \right) \end{aligned} \quad (186)$$

$$\begin{aligned} [\mathbf{q}'_-^{[N-1, 1]}]_i &= c_-^{[N-1, 1]} \cos \theta_-^{[N-1, 1]} \frac{1}{\sqrt{i(i+1)}} \left(\sum_{i=1}^i \bar{r}'_i - i \bar{r}'_{i+1} \right) \\ &+ c_-^{[N-1, 1]} \sin \theta_-^{[N-1, 1]} \frac{1}{\sqrt{i(i+1)(N-2)}} \left(\left[\sum_{l=2}^i \sum_{k=1}^{l-1} \bar{\gamma}'_{kl} + \sum_{k=1}^i \sum_{l=k+1}^N \bar{\gamma}'_{kl} \right] \right. \\ &\quad \left. - i \left[\sum_{k=1}^i \bar{\gamma}'_{k, i+1} + \sum_{l=i+2}^N \bar{\gamma}'_{i+1, l} \right] \right) \end{aligned} \quad (187)$$

$$[\mathbf{q}'^{[N-2, 2]}]_{ij} = c^{[N-2, 2]} \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left(\sum_{k=1}^i \widehat{\mathbf{r}}'_k - i \widehat{\mathbf{r}}'_{i+1} \right) \cdot \left(\sum_{j'=1}^{j-1} \widehat{\mathbf{r}}'_{j'} - (j-3) \widehat{\mathbf{r}}'_j \right). \quad (188)$$

9.3 The Motions Associated with the Normal Modes.

From Eqs. (108), (109), (110), (111), (112), (128), (144) and (180)

$$\mathbf{y} = \begin{pmatrix} \mathbf{r} \\ \gamma \end{pmatrix} = \mathbf{y}_\infty + \sum_{\alpha=\left\{\begin{smallmatrix} [N], \\ [N-1, 1] \end{smallmatrix}\right\}} \sum_{\xi} \sum_{\tau=\pm} \begin{pmatrix} \tau \mathbf{r}_\xi^\alpha \\ \tau \gamma_\xi^\alpha \end{pmatrix} + \sum_{\xi} \begin{pmatrix} \mathbf{0} \\ \gamma_\xi^{[N-2, 2]} \end{pmatrix}, \quad (189)$$

where \mathbf{y}_∞ is given by Eq. (109). The ξ sum for the $[N]$ species only includes one term and $+\mathbf{r}^{[N]}$, $+\gamma^{[N]}$, $-\mathbf{r}^{[N]}$ and $-\gamma^{[N]}$ are identified in Paper I. For the $[N-1, 1]$ species $1 \leq \xi \leq N-1$, and so we have

$$(+r_\xi^{[N-1, 1]})_i = -\bar{a}_{ho} \sqrt{\frac{D^3}{\xi(\xi+1)}} \frac{\sin \theta_-^{[N-1, 1]}}{s(\theta^{[N-1, 1]}) c_+^{[N-1, 1]}} [\mathbf{q}'_+^{[N-1, 1]}]_\xi (\Theta_{\xi-i+1} - \xi \delta_{\xi+1, i}), \quad (190)$$

$$\begin{aligned} (+\gamma_\xi^{[N-1, 1]})_{ij} &= \frac{1}{\sqrt{\xi(\xi+1)(N-2)D}} \frac{\cos \theta_-^{[N-1, 1]}}{s(\theta^{[N-1, 1]}) c_+^{[N-1, 1]}} [\mathbf{q}'_+^{[N-1, 1]}]_\xi \times \\ &\times \left((\Theta_{\xi-i+1} [\mathbf{1}_{\mathbf{r}'}]_{ij} + \Theta_{\xi-j+1} [\mathbf{1}_{\mathbf{r}'}]_{ij}) - \xi (\delta_{\xi+1, i} [\mathbf{1}_{\mathbf{r}'}]_{ij} + \delta_{\xi+1, j} [\mathbf{1}_{\mathbf{r}'}]_{ij}) \right), \end{aligned} \quad (191)$$

$$(-r_\xi^{[N-1, 1]})_i = \bar{a}_{ho} \sqrt{\frac{D^3}{\xi(\xi+1)}} \frac{\sin \theta_+^{[N-1, 1]}}{s(\theta^{[N-1, 1]}) c_-^{[N-1, 1]}} [\mathbf{q}'_-^{[N-1, 1]}]_\xi (\Theta_{\xi-i+1} - \xi \delta_{\xi+1, i}), \quad (192)$$

$$\begin{aligned} (-\gamma_\xi^{[N-1, 1]})_{ij} &= -\frac{1}{\sqrt{\xi(\xi+1)(N-2)D}} \frac{\cos \theta_+^{[N-1, 1]}}{s(\theta^{[N-1, 1]}) c_-^{[N-1, 1]}} [\mathbf{q}'_-^{[N-1, 1]}]_\xi \times \\ &\times \left((\Theta_{\xi-i+1} [\mathbf{1}_{\mathbf{r}'}]_{ij} + \Theta_{\xi-j+1} [\mathbf{1}_{\mathbf{r}'}]_{ij}) - \xi (\delta_{\xi+1, i} [\mathbf{1}_{\mathbf{r}'}]_{ij} + \delta_{\xi+1, j} [\mathbf{1}_{\mathbf{r}'}]_{ij}) \right). \end{aligned} \quad (193)$$

For the $[N-2, 2]$ species ξ runs over the set $\{k, l : \forall 1 \leq k \leq l-2 \text{ and } k+2 \leq l \leq N\}$ and so

$$\begin{aligned} (\gamma_{kl}^{[N-2, 2]})_{ij} &= \frac{1}{\sqrt{k(k+1)(l-3)(l-2)D}} \frac{1}{c^{[N-2, 2]}} [\mathbf{q}'^{[N-2, 2]}]_{kl} \times \\ &\times \left((\Theta_{k-i+1} - k \delta_{k+1, i})(\Theta_{l-j} - (l-3) \delta_{lj}) + \right. \\ &\left. + (\Theta_{k-j+1} - k \delta_{k+1, j})(\Theta_{l-i} - (l-3) \delta_{li}) \right). \end{aligned} \quad (194)$$

10 Summary.

In this paper we have completed the derivation, begun in Paper I, of the lowest-order DPT S -wave wave function of a correlated quantum confined system under spherical confinement with weak, intermediate or strong interparticle interactions. Remarkably, it is a largely analytic approach, yielding analytic expressions for energies, frequencies and wave functions (also density profiles). The achievement of analytic results is not due to a simplified description of the two-body interaction, but rather to the high degree of symmetry of the zeroth-order configuration in which every particle is equidistant and equiangular from every other particle in a high dimensional space. This symmetry allows us to use group theoretic methods rather than numerical techniques to account individually for each two-body interaction. The resulting simplification is

remarkable resulting in analytic formulas with N as a simple parameter as well as a stunning reduction in the number of normal modes. Even the zeroth-order result contains correlation effects as demonstrated by the interparticle angle cosine of the Lewis structure, $\overline{\gamma}_\infty$, which differs significantly from its mean-field, i.e. uncorrelated, value of zero.

We have obtained the normal modes and wave functions to lowest order using the FG method[13] which directly relates the structure of the Schrödinger equation to normal-mode coordinates describing the fundamental motions of the system (Eqs. (27) - (33)).

However, since DPT is a beyond mean-field treatment of the interacting N -body problem, where N may be large and where the $N(N+1)/2$ interactions can be strong, this is still a formidable problem. In particular there are $P = N(N+1)/2$ normal modes, and up to P distinct frequencies to calculate. However, the symmetry of the Lewis structure allows an enormous simplification in the calculation of frequencies and normal modes. Since the Lewis structure is invariant under interchange of particles, it satisfies an S_N symmetry. The full D -dimensional Hamiltonian as well as the Hamiltonian for the zeroth-order wave function are invariant under particle interchange, and thus invariant under S_N . This symmetry results, in fact, in only five distinct frequencies, a remarkable reduction in the number P of possible distinct frequencies. It also provides an immense simplification in the calculation of the normal mode coordinates.

We note that the S_N invariance of Eq. (27) means that the \mathbf{F} , \mathbf{G} and \mathbf{FG} matrices of Eqs. (27 - 31) are invariant under S_N . This implies that the eigenvectors \mathbf{b} and so the normal mode coordinates transform under irreducible representations of S_N . The coordinates \bar{r}'_i and $\bar{\gamma}'_{ij}$ transform *reducibly* under S_N ; however using the theory of group characters one can show that the \bar{r}'_i are reducible to one one-dimensional $[N]$ irreducible representation of S_N and one $(N-1)$ -dimensional $[N-1, 1]$ irreducible representation of S_N , while the $\bar{\gamma}'_{ij}$ are reducible to one one-dimensional $[N]$ irreducible representation of S_N , one $(N-1)$ -dimensional $[N-1, 1]$ irreducible representation of S_N and one $N(N-3)/2$ -dimensional $[N-2, 2]$ irreducible representation of S_N . Since the normal coordinates are linear combinations of the internal coordinates \bar{r}'_i and $\bar{\gamma}'_{ij}$ (Eqs. (21) - (23) and (28)), the normal coordinate set is comprised of two one-dimensional $[N]$ irreducible representations of S_N two $(N-1)$ -dimensional $[N-1, 1]$ irreducible representations of S_N and one entirely angular $N(N-3)/2$ -dimensional $[N-2, 2]$ irreducible representation of S_N .

This group theoretic information provides an immense simplification in the calculation of the normal mode coordinates through the use of symmetry coordinates[13]. We have determined the normal coordinates and distinct frequencies in a three-step process:

- a). We define sets of primitive irreducible coordinates having the simplest functional form possible subject to the requirement of transforming under particular non-orthogonal irreducible representations of S_N . For the $\bar{\mathbf{r}}'$ sector we define two sets of linear combinations of elements of the $\bar{\mathbf{r}}'$ vector which transform under non-orthogonal $[N]$ and $[N-1, 1]$ irreducible representations of S_N . We then derive two sets of linear combinations of elements of the $\bar{\boldsymbol{\gamma}}'$ vector which transform under exactly these same two irreducible representations of S_N . Finally we define a set of linear

combinations of elements of $\overline{\gamma}'$ which transform under a particular non-orthogonal $[N - 2, 2]$ irreducible representation of S_N .

- b). Using linear combinations within each set of primitive irreducible coordinates, we determine symmetry coordinates defined to transform under *orthogonal* irreducible representations of S_N . Care is taken to ensure that this transformation to the symmetry coordinates preserves the identity of equivalent representations in the \overline{r}' and $\overline{\gamma}'$ sectors. We choose one of the symmetry coordinates to be a single primitive irreducible coordinate, the simplest functional form possible under the requirement that it transforms irreducibly under S_N . The next symmetry coordinate is chosen to be composed of two primitive irreducible coordinates and so on. Thus the complexity of the symmetry coordinates is minimized, building up slowly as symmetry coordinates are added.
- c). The \mathbf{FG} matrix, originally expressed in the \overline{r}' and $\overline{\gamma}'$ basis, is now expressed in symmetry coordinates resulting in a stunning simplification. The $P \times P$ eigenvalue equation of Eq. (29) is reduced to one 2×2 eigenvalue equation for the $[N]$ sector, $N - 1$ identical 2×2 eigenvalue equations for the $[N - 1, 1]$ sector and $N(N - 3)/2$ identical 1×1 eigenvalue equations for the $[N - 2, 2]$ sector. For the $[N]$ and $[N - 1, 1]$ sectors, the 2×2 structure allows for mixing of the \overline{r}' and $\overline{\gamma}'$ symmetry coordinates in the normal coordinates (see Eq. (98)). The 1×1 structure of the equations in the $[N - 2, 2]$ sector reflects the absence of \overline{r}' symmetry coordinates in this sector, i.e. the $[N - 2, 2]$ normal modes are entirely angular.

11 Conclusions.

The increasing interest in creating systems controlled by quantum confinement is resulting in new interest and new demands on the N -body techniques of quantum physics and chemistry, originally developed for atoms and molecules. Mean-field treatments, such as the Hartree-Fock method in atomic physics and the Gross-Pitaevskii method for Bose-Einstein condensates, do not include correlation effects, and therefore fail for systems under tight confinement or strong interaction. These new systems, with a few hundred to millions of particles, present serious challenges for existing N -body methods, most of which were developed with small systems in mind.

Dimensional perturbation theory directly addresses these issues. Since the perturbation parameter is the dimensionality of space it is not limited to weak or strong interparticle interactions. Its formulation allows the symmetry of the problem to be exploited to the highest degree, enabling solutions for large N systems to be obtained with a minimum of numerical computation. In fact, dimensional perturbation theory for such systems produces analytic results that are a function of N . This means essentially that results for any N are obtained from a single calculation[2, 3].

Almost all past work using dimensional perturbation theory has focused on *energies* with little attention given to the difficult task of obtaining wave functions, even at lowest order. In Paper I we began the derivation

of the normal mode coordinates of the lowest-order wave function. The current paper completes this work. With the normal-mode coordinates of the zeroth-order wave function at hand, many other properties of the system beyond low-order energies become accessible. For macroscopic quantum confined systems the density profile is an experimentally accessible observable, and to lowest order may be calculated analytically from the zeroth-order wave function. The fact that it is an analytic function of N , means that the density profile is obtained for any N in a single calculation. The normal mode coordinates directly relate to the nature of the motions of excited states of the system which are also experimentally accessible for macroscopic quantum confined systems. Expectation values may be calculated, as may transition matrix elements. The fact that dimensional perturbation theory is a beyond-mean-field method means that such interesting properties may be derived for weakly, intermediate and strongly interacting systems, the latter two appearing in experiments with low- D or large- N systems as well as systems with strong interparticle interactions such as is the case with Feshbach resonances in Bose-Einstein condensates[5]. Knowing the zeroth-order wave function is a precursor to calculating higher-order results.

Almost all confining potentials for quantum confined systems in the lab currently have cylindrical symmetry. These include condensates confined in a cylindrical potential as well as axially symmetric quantum dots, two-dimensional electronic systems in a corbino disk geometry and rotating superfluid helium systems. One can extend the dimensional perturbation approach to handle such systems with axial, as opposed to spherical symmetry.

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A Calculation of $[\sigma_{[N-1, 1]}^G]_{X'_1, X'_2}$, $[\sigma_{[N-2, 2]}^G]_{\bar{\gamma}', \bar{\gamma}'}$, $[\sigma_{[N-1, 1]}^{FG}]_{X'_1, X'_2}$ and $[\sigma_{[N-2, 2]}^{FG}]_{\bar{\gamma}', \bar{\gamma}'}$, the reduced G and FG matrix elements in the symmetry-coordinate basis.

In this appendix we use the $W_{\mathbf{X}'}^\alpha$ matrices ($\alpha = [N-1, 1], [N-2, 2], \mathbf{X}' = \bar{\mathbf{r}}'$ or $\bar{\gamma}'$) to calculate the reduced G and FG matrix elements, $[\sigma_\alpha^G]_{X'_1, X'_2}$ and $[\sigma_\alpha^{FG}]_{X'_1, X'_2}$, using Eq. (85):

$$[\sigma_\alpha^Q]_{X'_1, X'_2} = (W_{\mathbf{X}'_1}^\alpha)_\xi Q_{X'_1 X'_2} [(W_{\mathbf{X}'_2}^\alpha)_\xi]^T, \quad (\text{A1})$$

where $Q = G$ or FG and ξ is a row label. Notice that $[\sigma_\alpha^Q]_{X'_1, X'_2}$ on the left-hand side of Eq. (A1) should be independent of the row label ξ on the right hand side of the equation. This is a strong check on the correctness of our calculations.

A.1 The Matrix Elements $[\sigma_{[N-1, 1]}^G]_{x'_1, x'_2}$ and $[\sigma_{[N-1, 1]}^{FG}]_{x'_1, x'_2}$

Equations (128) and Eq. (144) read

$$[W_{\bar{r}'}^{[N-1, 1]}]_{ik} = \frac{1}{\sqrt{i(i+1)}} \left(\sum_{m=1}^i \delta_{mk} - i\delta_{i+1, k} \right) = \frac{1}{\sqrt{i(i+1)}} (\Theta_{i-k+1} - i\delta_{i+1, k}) \quad (\text{A2})$$

and

$$\begin{aligned} & [W_{\bar{\gamma}'}^{[N-1, 1]}]_{i, kl} \\ &= \frac{1}{\sqrt{i(i+1)(N-2)}} \left(\sum_{m=1}^i (\delta_{mk} [\mathbf{1}_{\bar{r}'}]_l + \delta_{ml} [\mathbf{1}_{\bar{r}'}]_k) - i(\delta_{i+1, k} [\mathbf{1}_{\bar{r}'}]_l + \delta_{i+1, l} [\mathbf{1}_{\bar{r}'}]_k) \right), \end{aligned} \quad (\text{A3})$$

where $1 \leq k < l \leq N$ and $1 \leq i \leq N-1$. In this case the row index $\xi = i$. Thus from Eqs. (46), (A1), (A2) and (A3) we obtain:

$$\begin{aligned} [\sigma_{[N-1, 1]}^G]_{\bar{r}', \bar{r}'} &= \sum_{j,k=1}^N [W_{\bar{r}'}^{[N-1, 1]}]_{ij} [\mathbf{G}_{\bar{r}'\bar{r}'}]_{jk} [(W_{\bar{r}'}^{[N-1, 1]})^T]_{ki} \\ &= \frac{1}{i(i+1)} \sum_{j,k=1}^N \left(\sum_{p=1}^i \delta_{pj} - \delta_{i+1, j} \right) (\tilde{a}' \delta_{jk}) \left(\sum_{p'=1}^i \delta_{p'k} - i\delta_{i+1, k} \right) \\ &= \frac{\tilde{a}'}{i(i+1)} \sum_j \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1, j} \right) \left(\sum_{p'=1}^i \delta_{p'j} - i\delta_{i+1, j} \right) \\ &= \frac{\tilde{a}'}{i(i+1)} \left[\sum_{p=1}^i \sum_{p'=1}^i \delta_{pp'} - i \sum_{p=1}^i \delta_{p, i+1} - i \sum_{p'}^i \delta_{i+1, p'} + i^2 \delta_{i+1, i+1} \right] \\ &= \frac{\tilde{a}'}{i(i+1)} [i + i^2] \\ &= \tilde{a}' \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} [\sigma_{[N-1, 1]}^G]_{\bar{r}', \bar{\gamma}'} &= \sum_{j=1}^N \sum_{l=2}^N \sum_{k=1}^{l-1} [W_{\bar{r}'}^{[N-1, 1]}]_{ij} [\mathbf{G}_{\bar{r}'\bar{\gamma}'}]_{j, kl} [(W_{\bar{\gamma}'}^{[N-1, 1]})^T]_{kl, i} \\ &= 0 \end{aligned} \quad (\text{A5})$$

$$\begin{aligned} [\sigma_{[N-1, 1]}^G]_{\bar{\gamma}', \bar{r}'} &= \sum_{k=2}^N \sum_{j=1}^{k-1} \sum_{l=1}^N [W_{\bar{\gamma}'}^{[N-1, 1]}]_{i, jk} [\mathbf{G}_{\bar{\gamma}'\bar{r}'}]_{j, kl} [(W_{\bar{r}'}^{[N-1, 1]})^T]_{li} \\ &= 0 \end{aligned} \quad (\text{A6})$$

and

$$\begin{aligned}
[\sigma_{[N-1, 1]}^G]_{\vec{\gamma}', \vec{\gamma}'} &= [W_{\vec{\gamma}'}^{[N-1, 1]}] [G_{\vec{\gamma}' \vec{\gamma}'}] [W_{\vec{\gamma}'}^{[N-1, 1]}]^T \\
&= [W_{\vec{\gamma}'}^{[N-1, 1]}] [\tilde{g}' I_M + \tilde{h}' R^T R] [W_{\vec{\gamma}'}^{[N-1, 1]}]^T \\
&= \tilde{g}' [W_{\vec{\gamma}'}^{[N-1, 1]}] [W_{\vec{\gamma}'}^{[N-1, 1]}]^T + \tilde{h}' [W_{\vec{\gamma}'}^{[N-1, 1]}] R^T R [W_{\vec{\gamma}'}^{[N-1, 1]}]^T \\
&= \tilde{g}' + \tilde{h}' \sum_{k=2}^N \sum_{j=1}^{k-1} \sum_{m=2}^N \sum_{l=1}^{m-1} [W_{\vec{\gamma}'}^{[N-1, 1]}]_{i,jk} [R^T R]_{jk,lm} [(W_{\vec{\gamma}'}^{[N-1, 1]}]^T)_{lm,i} \\
&= \tilde{g}' + \frac{\tilde{h}'}{i(i+1)(N-2)} \sum_{k=2}^N \sum_{j=1}^{k-1} \sum_{m=2}^N \sum_{l=1}^{m-1} \left(\sum_{p=1}^i (\delta_{pj} + \delta_{pk}) - i(\delta_{i+1,j} + \delta_{i+1,k}) \right) \\
&\quad \left((\delta_{jl} + \delta_{kl}) + (\delta_{jm} + \delta_{km}) \right) \left(\sum_{p'=1}^i (\delta_{lp'} + \delta_{mp'}) - i(\delta_{l,i+1} + \delta_{m,i+1}) \right). \tag{A7}
\end{aligned}$$

Using $\sum_{m=2}^N \sum_{l=1}^{m-1} = \frac{1}{2} \sum_{m=1}^N \sum_{l=1}^N - \frac{1}{2} \sum_{l=1}^N \delta_{ml}$ in Eq. (A7), and summing over m yields:

$$\begin{aligned}
[\sigma_{[N-1, 1]}^G]_{\vec{\gamma}', \vec{\gamma}'} &= \tilde{g}' + \frac{\tilde{h}'}{2i(i+1)(N-2)} \sum_{k=2}^N \sum_{j=1}^{k-1} \sum_{l=1}^N \left(\sum_{p=1}^i (\delta_{pj} + \delta_{pk}) - i(\delta_{i+1,j} + \delta_{i+1,k}) \right) \\
&\quad \left(2(\delta_{jl} + \delta_{kl}) \right) \left(N \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) + \sum_{m=1}^N \left(\sum_{p'=1}^i \delta_{mp'} - i\delta_{m,i+1} \right) \right. \\
&\quad \left. - 2 \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) \right). \tag{A8}
\end{aligned}$$

Then using $\sum_{m=1}^N (\sum_{p'=1}^i \delta_{mp'} - i\delta_{m,i+1}) = 0$ and $\sum_{k=2}^N \sum_{j=1}^{k-1} = \frac{1}{2} \sum_{k=1}^N \sum_{j=1}^N - \frac{1}{2} \sum_{k=1}^N \delta_{jk}$ in Eq. (A8), we find:

$$\begin{aligned}
[\sigma_{[N-1, 1]}^G]_{\vec{\gamma}', \vec{\gamma}'} &= \tilde{g}' + \frac{\tilde{h}'}{4i(i+1)(N-2)} \left[\sum_{k,j,l=1}^N \left(\left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) + \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \right) \right. \\
&\quad \left. (4\delta_{jl}) \left((N-2) \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) \right) \right. \\
&\quad \left. - 2 \sum_{j,l=1}^N \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) (4\delta_{jl}) \left((N-2) \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) \right) \right] \\
&= \tilde{g}' + \frac{\tilde{h}'}{i(i+1)} \left[\sum_{j,l=1}^N \left(N \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) + \sum_{k=1}^N \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \right. \right. \\
&\quad \left. \left. - 2 \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) \right) (\delta_{jl}) \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) \right] \\
&= \tilde{g}' + \frac{\tilde{h}'(N-2)}{i(i+1)} \sum_{j,l=1}^N \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) (\delta_{jl}) \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) \\
&= \tilde{g}' + \frac{\tilde{h}'(N-2)}{i(i+1)} (i(i+1)) \\
&= \tilde{g}' + (N-2)\tilde{h}' \tag{A9}
\end{aligned}$$

Thus we obtain for the reduced \mathbf{G} matrix in the $[N-1, 1]$ symmetry-coordinate basis:

$$\sigma_{[N-1, 1]}^{\mathbf{G}} = \begin{pmatrix} [\sigma_{[N-1, 1]}^{\mathbf{G}}]_{\bar{r}', \bar{r}'} = \tilde{a}' & [\sigma_{[N-1, 1]}^{\mathbf{FG}}]_{\bar{r}', \bar{\gamma}'} = 0 \\ [\sigma_{[N-1, 1]}^{\mathbf{G}}]_{\bar{\gamma}', \bar{r}'} = 0 & [\sigma_{[N-1, 1]}^{\mathbf{G}}]_{\bar{\gamma}', \bar{\gamma}'} = (\tilde{g}' + (N-2)\tilde{h}') \end{pmatrix}. \quad (\text{A10})$$

Now letting $\mathbf{Q} = \mathbf{FG}$ and using Eqs. (44), (A1), (A2) and (A3) we can derive:

$$\begin{aligned} [\sigma_{[N-1, 1]}^{\mathbf{FG}}]_{\bar{r}', \bar{r}'} &= \sum_{j,k=1}^N [W_{\bar{r}'}^{[N-1, 1]}]_{ij} [\mathbf{FG}_{\bar{r}'\bar{r}'}]_{jk} [(W_{\bar{r}'}^{[N-1, 1]})^T]_{ki} \\ &= \frac{1}{i(i+1)} \sum_{j,k=1}^N \left(\sum_{p=1}^i \delta_{pj} - \delta_{i+1,j} \right) (\tilde{a}\delta_{jk} + \tilde{b}[1_{\bar{r}'\bar{r}'}]_{jk}) \left(\sum_{p'=1}^i \delta_{p'k} - i\delta_{i+1,k} \right) \\ &= \frac{1}{i(i+1)} \left[\sum_j \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) \tilde{a} \left(\sum_{p'=1}^i \delta_{p'j} - i\delta_{i+1,j} \right) \right. \\ &\quad \left. + \sum_j \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) \tilde{b} \sum_{k=1}^N \left(\sum_{p'=1}^i \delta_{p'k} - i\delta_{i+1,k} \right) \right] \\ &= \tilde{a} \end{aligned} \quad (\text{A11})$$

$$\begin{aligned} [\sigma_{[N-1, 1]}^{\mathbf{FG}}]_{\bar{r}', \bar{\gamma}'} &= \sum_{j=1}^N \sum_{l=2}^N \sum_{k=1}^{l-1} [W_{\bar{r}'}^{[N-1, 1]}]_{ij} [\mathbf{FG}_{\bar{r}'\bar{\gamma}'}]_{j,kl} [(W_{\bar{\gamma}'}^{[N-1, 1]})^T]_{kl,i} \\ &= \frac{1}{i(i+1)\sqrt{N-2}} \sum_{j=1}^N \sum_{l=2}^N \sum_{k=1}^{l-1} \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) (\tilde{e}(\delta_{jk} + \delta_{jl}) + \tilde{f}) \\ &\quad \times \left(\sum_{p'=1}^i (\delta_{kp'} + \delta_{lp'}) - i(\delta_{k,i+1} + \delta_{l,i+1}) \right) \\ &= \frac{1}{2i(i+1)\sqrt{N-2}} \left[\sum_{j,l,k=1}^N \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) (\tilde{e}(\delta_{jk} + \delta_{jl}) + \tilde{f}) \right. \\ &\quad \times \left(\sum_{p'=1}^i (\delta_{kp'} + \delta_{lp'}) - i(\delta_{k,i+1} + \delta_{l,i+1}) \right) \\ &\quad \left. - 2 \left(\sum_{j,k=1}^N \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) (2\tilde{e}\delta_{jk} + \tilde{f}) \left(\sum_{p'=1}^i \delta_{kp'} - i\delta_{k,i+1} \right) \right) \right]. \end{aligned} \quad (\text{A12})$$

Using $\sum_{j=1}^N (\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j}) = 0$ in Eq. (A12), the term involving \tilde{f} is zero. Summing over j then yields:

$$\begin{aligned} [\sigma_{[N-1, 1]}^{\mathbf{FG}}]_{\bar{r}', \bar{\gamma}'} &= \frac{1}{2i(i+1)\sqrt{N-2}} \left[\sum_{k,l=1}^N \left(\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) + \left(\sum_{p=1}^N \delta_{pl} - i\delta_{i+1,l} \right) \right) \right. \\ &\quad \times \tilde{e} \left(\left(\sum_{p'=1}^i \delta_{kp'} - i\delta_{k,i+1} \right) + \left(\sum_{p'=1}^N \delta_{lp'} - i\delta_{l,i+1} \right) \right) \\ &\quad \left. - 2 \left(\sum_{k=1}^N \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) (2\tilde{e}) \left(\sum_{p'=1}^i \delta_{kp'} - i\delta_{k,i+1} \right) \right) \right]. \end{aligned} \quad (\text{A13})$$

The term involving $2\tilde{e}$ in Eq. (A13) gives $4\tilde{e}i(i+1)$ (see Eq. (A4)) leaving

$$\begin{aligned}
[\sigma_{[N-1, \mathbf{1}]}^{FG}]_{\bar{r}', \bar{\gamma}'} &= \frac{1}{2i(i+1)\sqrt{N-2}} \left[\tilde{e} \sum_{k,l=1}^N \left(\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^i \delta_{kp'} - i\delta_{k,i+1} \right) \right. \right. \\
&\quad + \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) \\
&\quad + \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^i \delta_{kp'} - i\delta_{k,i+1} \right) \\
&\quad \left. + \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) - 4\tilde{e}i(i+1) \right] \\
&= \frac{1}{2i(i+1)\sqrt{N-2}} \left[N \sum_{k=1}^N \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^i \delta_{kp'} - i\delta_{k,i+1} \right) \right. \\
&\quad \left. + N \sum_{l=1}^N \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) - 4i(i+1) \right] \\
&= \frac{1}{2i(i+1)\sqrt{N-2}} [2Ni(i+1) - 4i(i+1)] \\
&= \frac{\tilde{e}}{\sqrt{N-2}} [N-2] \\
&= \sqrt{N-2} \tilde{e}.
\end{aligned} \tag{A14}$$

An analogous calculation yields

$$[\sigma_{[N-1, \mathbf{1}]}^{FG}]_{\bar{\gamma}', \bar{r}'} = \sqrt{N-2} \tilde{c}. \tag{A15}$$

Finally from Eq. (44)

$$\begin{aligned}
[\sigma_{[N-1, \mathbf{1}]}^{FG}]_{\bar{\gamma}', \bar{\gamma}'} &= [W_{\bar{\gamma}'}^{[N-1, \mathbf{1}]} [\mathbf{F} \mathbf{G}_{\bar{\gamma}' \bar{\gamma}'}] W_{\bar{\gamma}'}^{[N-1, \mathbf{1}]}]^T \\
&= [W_{\bar{\gamma}'}^{[N-1, \mathbf{1}]} [\tilde{g}I_M + \tilde{h}R^T R + \tilde{t}J_M] W_{\bar{\gamma}'}^{[N-1, \mathbf{1}]}]^T.
\end{aligned} \tag{A16}$$

The first two terms in the center brackets are evaluated identically to similar terms for $[\sigma_{[N-1, \mathbf{1}]}^G]_{\bar{\gamma}', \bar{\gamma}'}$ and

yield $\tilde{g} + (N - 2)\tilde{h}$. The term involving $\tilde{l}J_M$ is zero as shown below:

$$\begin{aligned}
[W_{\vec{\gamma}'}^{[N-1, 1]} \tilde{l} J_M [W_{\vec{\gamma}'}^{[N-1, 1]}]^T &= \frac{1}{i(i+1)(N-2)} \left[\sum_{k=2}^N \sum_{j=1}^{k-1} \sum_{m=2}^N \sum_{l=1}^{m-1} \left(\sum_{p=1}^i (\delta_{pj} + \delta_{pk}) - i(\delta_{i+1,j} + \delta_{i+1,k}) \right) \right. \\
&\quad \left. \times \tilde{l} \left(\sum_{p'=1}^i (\delta_{lp'} + \delta_{mp'}) - i(\delta_{l,i+1} + \delta_{m,i+1}) \right) \right] \\
&= \frac{1}{2} \frac{1}{i(i+1)(N-2)} \left[\left[\sum_{k,j=1}^N \left(\left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) + \left(\sum_{p=1}^N \delta_{pk} - i\delta_{i+1,k} \right) \right) \right. \right. \\
&\quad \left. \left. - 2 \sum_{j=1}^N \left(\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j} \right) \right] \tilde{l} \left(\sum_{m=2}^N \sum_{l=1}^{m-1} \left(\sum_{p'=1}^i \delta_{lp'} - i\delta_{l,i+1} \right) \right. \right. \\
&\quad \left. \left. + \left(\sum_{p'=1}^i \delta_{mp'} - i\delta_{m,i+1} \right) \right) \right] \\
&= 0,
\end{aligned} \tag{A17}$$

where we have used $\sum_{j=1}^N (\sum_{p=1}^i \delta_{pj} - i\delta_{i+1,j}) = 0$.

Thus we obtain

$$\sigma_{[N-1, 1]}^{FG} = \begin{pmatrix} [\sigma_{[N-1, 1]}^{FG}]_{\vec{r}', \vec{r}'} = \tilde{a} & [\sigma_{[N-1, 1]}^{FG}]_{\vec{r}', \vec{\gamma}'} = \sqrt{N-2} \tilde{e} \\ [\sigma_{[N-1, 1]}^{FG}]_{\vec{\gamma}', \vec{r}'} = \sqrt{N-2} \tilde{c} & [\sigma_{[N-1, 1]}^{FG}]_{\vec{\gamma}', \vec{\gamma}'} = (\tilde{g} + (N-2)\tilde{h}) \end{pmatrix}, \tag{A18}$$

for the reduced FG matrix in the $[N-1, 1]$ symmetry-coordinate basis.

A.2 The Matrix Elements $[\sigma_{[N-2, 2]}^G]_{\vec{\gamma}', \vec{\gamma}'}$ and $[\sigma_{[N-2, 2]}^{FG}]_{\vec{\gamma}', \vec{\gamma}'}$

From Eq. (180)

$$\begin{aligned}
[W_{\vec{\gamma}'}^{[N-2, 2]}]_{ij, mn} &= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left((\Theta_{i-m+1} - i\delta_{i+1,m})(\Theta_{j-n} - (j-3)\delta_{jn}) \right. \\
&\quad \left. + (\Theta_{i-n+1} - i\delta_{i+1,n})(\Theta_{j-m} - (j-3)\delta_{jm}) \right),
\end{aligned} \tag{A19}$$

where $2 \leq n \leq N$, $1 \leq m \leq n-1$, $1 \leq i \leq j-2$, $4 \leq j \leq N$ and (Eq. (124))

$$\begin{aligned}
\Theta_{\alpha-\beta} = \sum_{m=1}^{\alpha-1} \delta_{m,\beta} &= 1 \text{ when } \alpha - \beta > 0 \\
&= 0 \text{ when } \alpha - \beta \leq 0.
\end{aligned} \tag{A20}$$

In this case the row index ξ is the pair ij . Equations (A19) and (A20) give

$$\begin{aligned}
[W_{\vec{\gamma}'}^{[N-2, 2]}]_{ij, mn} &= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left(\left(\sum_{p=1}^i \delta_{pm} - i\delta_{i+1,m} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'n} - (j-3)\delta_{jn} \right) \right. \\
&\quad \left. + \left(\sum_{p=1}^i \delta_{pn} - i\delta_{i+1,n} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'm} - (j-3)\delta_{jm} \right) \right),
\end{aligned} \tag{A21}$$

and so from Eqs. (46), (A1) and (A21) we obtain

$$\begin{aligned}
[\sigma_{[N-2, 2]}^G]_{\tilde{\gamma}', \tilde{\gamma}'} &= [W_{\tilde{\gamma}'}^{[N-2, 2]}] [G_{\tilde{\gamma}' \tilde{\gamma}'}] [W_{\tilde{\gamma}'}^{[N-2, 2]}]^T \\
&= [W_{\tilde{\gamma}'}^{[N-2, 2]}] [\tilde{g}' I_M + \tilde{h}' R^T R] [W_{\tilde{\gamma}'}^{[N-2, 2]}]^T \\
&= \tilde{g}' [W_{\tilde{\gamma}'}^{[N-2, 2]}] [W_{\tilde{\gamma}'}^{[N-2, 2]}]^T + \tilde{h}' [W_{\tilde{\gamma}'}^{[N-2, 2]}] R^T R [W_{\tilde{\gamma}'}^{[N-2, 2]}]^T \\
&= \tilde{g}' + \tilde{h}' [W_{\tilde{\gamma}'}^{[N-2, 2]}] R^T R [W_{\tilde{\gamma}'}^{[N-2, 2]}]^T \\
&= \tilde{g}' + \tilde{h}' \sum_{l=2}^N \sum_{k=1}^{l-1} \sum_{n=2}^N \sum_{m=1}^{n-1} [W_{\tilde{\gamma}'}^{[N-2, 2]}]_{ij;kl} [R^T R]_{kl,mn} [(W_{\tilde{\gamma}'}^{[N-2, 2]})^T]_{mn,ij} \\
&= \tilde{g}' + \tilde{h}' \sum_{r=1}^N \left(\sum_{l=2}^N \sum_{k=1}^{l-1} [W_{\tilde{\gamma}'}^{[N-2, 2]}]_{ij;kl} (R^T)_{kl,r} \right) \left(\sum_{n=2}^N \sum_{m=1}^{n-1} (R)_{r,mn} [(W_{\tilde{\gamma}'}^{[N-2, 2]})^T]_{mn,ij} \right).
\end{aligned} \tag{A22}$$

We can show that the term involving \tilde{h}' is zero by performing the double sum $\sum_{l=2}^N \sum_{k=1}^{l-1}$:

$$\begin{aligned}
&\sum_{l=2}^N \sum_{k=1}^{l-1} [W_{\tilde{\gamma}'}^{[N-2, 2]}]_{ij;kl} (R^T)_{kl,r} \\
&= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \sum_{l=2}^N \sum_{k=1}^{l-1} \left(\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'l} - (j-3)\delta_{jl} \right) \right. \\
&\quad \left. + \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) \right) (\delta_{rk} + \delta_{rl}) \\
&= \frac{1}{2\sqrt{i(i+1)(j-3)(j-2)}} \left[\sum_{k,l=1}^N \left(\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'l} - (j-3)\delta_{jl} \right) \right. \right. \\
&\quad \left. \left. + \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) \right) (\delta_{rk} + \delta_{rl}) \right. \\
&\quad \left. - 2 \sum_{k=1}^N \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) (\delta_{rk}) \right].
\end{aligned} \tag{A23}$$

Summing over k and using the fact that $i \leq j-2$ in the last term we obtain:

$$\begin{aligned}
\sum_{l=2}^N \sum_{k=1}^{l-1} [W_{\tilde{\gamma}'}^{[N-2, 2]}]_{ij;kl} (R^T)_{kl,r} &= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left[\sum_{l=1}^N \left(\sum_{p=1}^i \delta_{pr} - i\delta_{i+1,r} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'l} - (j-3)\delta_{jl} \right) \right. \\
&\quad \left. + \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'r} - (j-3)\delta_{jr} \right) - 2 \left(\sum_{p=1}^i \delta_{pr} - i\delta_{i+1,r} \right) \right]
\end{aligned}$$

Then summing over l and using $\sum_{l=1}^N (\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l}) = 0$ along with $\sum_{l=1}^N (\sum_{p'=1}^{j-1} \delta_{p'l} - (j-3)\delta_{jl}) = 2$ one obtains

$$\begin{aligned}
\sum_{l=2}^N \sum_{k=1}^{l-1} [W_{\tilde{\gamma}'}^{[N-2, 2]}]_{ij;kl} (R^T)_{kl,r} &= \frac{1}{\sqrt{i(i+1)(j-3)(j-2)}} \left[2 \left(\sum_{p=1}^i \delta_{pr} - i\delta_{i+1,r} \right) - 2 \left(\sum_{p=1}^i \delta_{pr} - i\delta_{i+1,r} \right) \right] \\
&= 0.
\end{aligned} \tag{A24}$$

Thus from Eqs. (A22) and (A24)

$$[\sigma_{[N-2, 2]}^G]_{\bar{\gamma}', \bar{\gamma}'} = \tilde{g}'. \quad (\text{A25})$$

Similarly for the matrix element $[\sigma_{[N-2, 2]}^{FG}]_{\bar{\gamma}', \bar{\gamma}'}$ we obtain

$$\begin{aligned} [\sigma_{[N-2, 2]}^{FG}]_{\bar{\gamma}', \bar{\gamma}'} &= [W_{\bar{\gamma}'}^{[N-2, 2]}] [FG_{\bar{\gamma}'\bar{\gamma}'}] [W_{\bar{\gamma}'}^{[N-2, 2]}]^T \\ &= [W_{\bar{\gamma}'}^{[N-2, 2]}] [\tilde{g}I_M + \tilde{h}R^T R + \tilde{l}J_M] [W_{\bar{\gamma}'}^{[N-2, 2]}]^T \end{aligned} \quad (\text{A26})$$

The first two terms in the center bracket are evaluated identically to the analogous terms for $[\sigma_{[N-2, 2]}^G]_{\bar{\gamma}', \bar{\gamma}'}$ and from Eq. (A25) yield \tilde{g} . The term involving $\tilde{l}J_M$ is zero as shown below:

$$\begin{aligned} & [W_{\bar{\gamma}'}^{[N-2, 2]}] \tilde{l}J_M [W_{\bar{\gamma}'}^{[N-2, 2]}]^T \\ &= \sum_{l=2}^N \sum_{k=1}^{l-1} \sum_{n=2}^N \sum_{m=1}^{n-1} [W_{\bar{\gamma}'}^{[N-2, 2]}]_{ij,kl} \tilde{l} [(W_{\bar{\gamma}'}^{[N-2, 2]})^T]_{mn,ij} \\ &= \frac{1}{i(i+1)(j-3)(j-2)} \sum_{l=2}^N \sum_{k=1}^{l-1} \sum_{n=2}^N \sum_{m=1}^{n-1} \\ & \quad \left[\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'l} - (j-3)\delta_{jl} \right) + \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) \right] \\ & \quad \times \tilde{l} \left[\left(\sum_{p=1}^i \delta_{pm} - i\delta_{i+1,m} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'n} - (j-3)\delta_{jn} \right) + \left(\sum_{p=1}^i \delta_{pn} - i\delta_{i+1,n} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'm} - (j-3)\delta_{jm} \right) \right] \\ &= \frac{1}{2i(i+1)(j-3)(j-2)} \left[\sum_{l,k=1}^N \left(\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'l} - (j-3)\delta_{jl} \right) \right. \right. \\ & \quad \left. \left. + \left(\sum_{p=1}^i \delta_{pl} - i\delta_{i+1,l} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) \right) \right. \\ & \quad \left. - 2 \sum_{k=1}^N \left(\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) \right) \right] \\ & \quad \times \tilde{l} \left[\sum_{n=2}^N \sum_{m=1}^{n-1} \left(\sum_{p=1}^i \delta_{pm} - i\delta_{i+1,m} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'n} - (j-3)\delta_{jn} \right) \right. \\ & \quad \left. + \left(\sum_{p=1}^i \delta_{pn} - i\delta_{i+1,n} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'm} - (j-3)\delta_{jm} \right) \right]. \end{aligned} \quad (\text{A27})$$

Using $\sum_{k=1}^N (\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k}) = 0$ yields:

$$\begin{aligned}
& [W_{\vec{\gamma}'}^{[N-2, 2]}] \tilde{t} J_M [W_{\vec{\gamma}'}^{[N-2, 2]}]^T \\
&= \frac{-1}{i(i+1)(j-3)(j-2)} \left[\sum_{k=1}^N \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) \right] \\
&\quad \times \tilde{t} \left[\sum_{n,m=1}^N \frac{1}{2} \left(\left(\sum_{p=1}^i \delta_{pm} - i\delta_{i+1,m} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'n} - (j-3)\delta_{jn} \right) \right. \right. \\
&\quad \left. \left. + \left(\sum_{p=1}^i \delta_{pn} - i\delta_{i+1,n} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'm} - (j-3)\delta_{jm} \right) \right) \right. \\
&\quad \left. - \sum_{m=1}^N \left(\left(\sum_{p=1}^i \delta_{pm} - i\delta_{i+1,m} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'm} - (j-3)\delta_{jm} \right) \right) \right].
\end{aligned} \tag{A28}$$

Since $i \leq j-2$, $\left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \left(\sum_{p'=1}^{j-1} \delta_{p'k} - (j-3)\delta_{jk} \right) = \sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k}$ holds we obtain

$$\begin{aligned}
[W_{\vec{\gamma}'}^{[N-2, 2]}] \tilde{t} J_M [W_{\vec{\gamma}'}^{[N-2, 2]}]^T &= \frac{-1}{i(i+1)(j-3)(j-2)} \left[\sum_{k=1}^N \left(\sum_{p=1}^i \delta_{pk} - i\delta_{i+1,k} \right) \right] \\
&\quad \times \tilde{t} \left[\sum_{m=1}^N \left(\sum_{p=1}^i \delta_{pm} - i\delta_{i+1,m} \right) \right. \\
&\quad \left. - \sum_{m=1}^i \left(\sum_{p=1}^i \delta_{pm} - i\delta_{i+1,m} \right) \right] \\
&= 0
\end{aligned} \tag{A29}$$

Thus the reduced \mathbf{FG} matrix element in the symmetry-coordinate basis in the $[N-2, 2]$ sector is:

$$[\sigma_{[N-2, 2]}^{FG}]_{\vec{\gamma}', \vec{\gamma}'} = \tilde{g} \tag{A30}$$

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- [14] In Ref. [1], Eq. (35) would read

$$\begin{aligned}
\bar{E} &= \bar{E}_\infty + \delta \bar{E}_o + O(\delta^2) \\
&= V_{\text{eff}}(\bar{r}_\infty, \bar{\gamma}_\infty) + \delta \left\{ \sum_{\mu=\{\mathbf{0}^\pm, \mathbf{1}^\pm, \mathbf{2}^\pm\}} (n_\mu + \frac{d_\mu}{2}) \bar{\omega}_\mu + v_o \right\} + O(\delta^2), \tag{A31}
\end{aligned}$$

where n_μ is the total number of quanta in all the normal modes with the same frequency $\bar{\omega}_\mu$, i.e.

$$n_\mu = \sum_{n_\mu=0}^{\infty} n_\mu d_{\mu, n_\mu}. \tag{A32}$$

- [15] Ref. [9], p. 27.